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Si₁₀Cu₆N₄ Cage Hexacoppersilsesquioxanes Containing N Ligands: Synthesis, Structure, and High Catalytic Activity in Peroxide Oxidations

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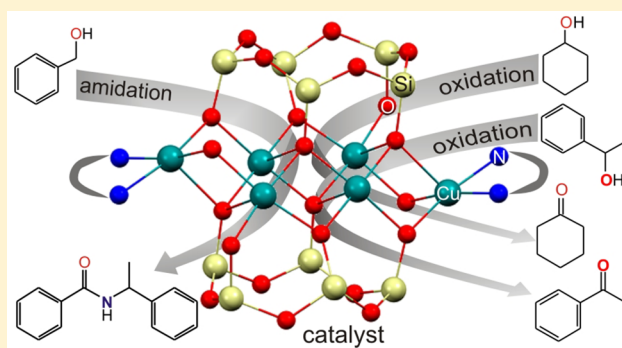
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ABSTRACT: The synthesis, composition, and catalytic properties of a new family of hexanuclear Cu(II)-based phenylsilsesquioxanes are described here. Structural studies of 17 synthesized compounds revealed the general principle underlying their molecular topology: viz., a central metal oxide layer consisting of two Cu₃ 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 H₃CO[−] (compound 8), or two CH₃COO[−] (compounds 9 and 14) anions. Complexes 1 and 10 exhibited a high activity in the oxidative amidation 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 cage-like compounds (polycyclic 3D structures with well-defined geometry) have attracted enormous attention from scientific groups due to their striking molecular topology¹ as well as their huge potential for practical applications.² These latter applications include, for example, intriguing cases of development of polymer science³ and medicine.⁴ A diversity of self-assembly procedures was elaborated for the construction of cage-like 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 (cage-like

metallsilsesquioxanes, CLMSs) has drawn special attention as attractive molecular architectures⁶ exhibiting unusual magnetic (spin glass behavior) effects⁷ and opportunities for the creation of inorganic materials⁸ or nanoparticles.⁹ In turn, great deal of attention has been devoted to the investigation of the catalytic activity of metallsilsesquioxanes.¹⁰ For example, their high activity was reported for such reactions of high demand as olefin¹¹ 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

activity of cage-like metallasilsesquioxanes in oxidative hydrocarbon functionalization¹⁷ and amidation¹⁸ reactions. Very recently, some of us presented the first example of the successful testing of CLMSs, including additional organic (phosphorus-based¹⁹) 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 CLMS²⁰ (complex with Cp*) synthesis as well as numerous types of other complexes: with carborane,²¹ acac,²² tricyclohexylphosphine,²³ cyclooctenyl,²⁴ methyl,²⁵ or silylamide²⁶ 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)amine²⁸ and bipy²⁹ 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 CuCl₂.³⁰ 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 nonanuclear³⁰ 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 CuCl₂ 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(C₁₀H₈N₂)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 CuCl₂ 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(C₁₀H₈N₂)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 CuCl₂ 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(C₁₀H₈N₂)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 CuCl₂ 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(C₁₀H₈N₂)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 CuCl₂ 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 $[(\text{PhSiO}_{1.5})_{10}(\text{CuO})_6(\text{HO}_{0.5})_2(\text{C}_{10}\text{H}_8\text{N}_2)_2]$: 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 $\text{PhSi}(\text{OMe})_3$, 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 $[(\text{PhSiO}_{1.5})_{10}(\text{CuO})_6(\text{HO}_{0.5})_2(\text{C}_{10}\text{H}_8\text{N}_2)_2]$: 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 $\text{PhSi}(\text{OMe})_3$, 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 $[(\text{PhSiO}_{1.5})_{10}(\text{CuO})_6(\text{HO}_{0.5})_2(\text{C}_{10}\text{H}_8\text{N}_2)_3]$: 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 $\text{PhSi}(\text{OMe})_3$, 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 $[(\text{PhSiO}_{1.5})_{10}(\text{CuO})_6(\text{CH}_3\text{O}_{0.5})_2(\text{C}_{10}\text{H}_8\text{N}_2)_2]$: 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 $\text{PhSi}(\text{OMe})_3$, 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 $[(\text{PhSiO}_{1.5})_{10}(\text{CuO})_6(\text{CH}_3\text{COO}_{0.5})_2(\text{C}_{10}\text{H}_8\text{N}_2)_2]$: 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 $\text{PhSi}(\text{OMe})_3$, 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 $[(\text{PhSiO}_{1.5})_{10}(\text{CuO})_6(\text{HO}_{0.5})_2(\text{C}_{12}\text{H}_8\text{N}_2)_2]$: 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 $\text{PhSi}(\text{OMe})_3$, 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 $[(\text{PhSiO}_{1.5})_{10}(\text{CuO})_6(\text{HO}_{0.5})_2(\text{C}_{12}\text{H}_8\text{N}_2)_2]$: 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 $\text{PhSi}(\text{OMe})_3$, 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

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 $[(\text{PhSiO}_{1.5})_{10}(\text{CuO})_6(\text{HO}_{0.5})_2(\text{C}_{12}\text{H}_8\text{N}_2)_2]$: 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 $\text{PhSi}(\text{OMe})_3$, 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 $[(\text{PhSiO}_{1.5})_{10}(\text{CuO})_6(\text{HO}_{0.5})_2(\text{C}_{12}\text{H}_8\text{N}_2)_2]$: 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 $\text{PhSi}(\text{OMe})_3$, 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 $[(\text{PhSiO}_{1.5})_{10}(\text{CuO})_6(\text{CH}_3\text{COO}_{0.5})_2(\text{C}_{12}\text{H}_8\text{N}_2)(\text{C}_{10}\text{H}_8\text{N}_2)]$: 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 $\text{PhSi}(\text{OMe})_3$, 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 $[(\text{PhSiO}_{1.5})_{10}(\text{CuO})_6(\text{HO}_{0.5})_2(\text{C}_{24}\text{H}_{16}\text{N}_2)_2]$: 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 $\text{PhSi}(\text{OMe})_3$, 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 $[(\text{PhSiO}_{1.5})_{10}(\text{CuO})_6(\text{HO}_{0.5})_2(\text{C}_{24}\text{H}_{16}\text{N}_2)_2]$: 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 $\text{PhSi}(\text{OMe})_3$, 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 $[(\text{PhSiO}_{1.5})_{10}(\text{CuO})_6(\text{HO}_{0.5})_2(\text{C}_{24}\text{H}_{16}\text{N}_2)_2]$: 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 ($U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for the CH_3 groups and $1.2U_{\text{eq}}(\text{C})$ for the other groups). All calculations were carried out using the SHELXL^{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.

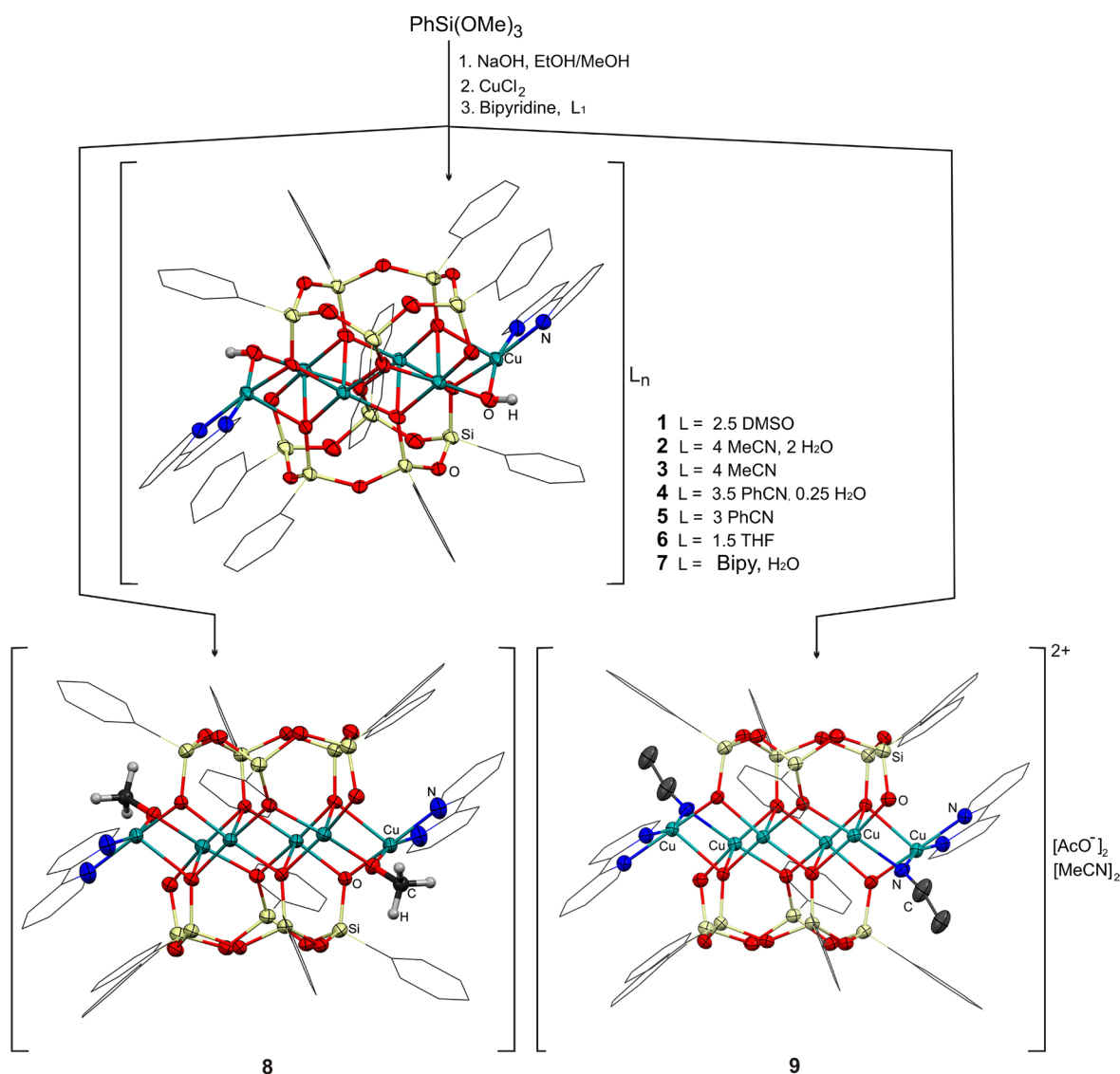


Figure 1. General scheme of synthesis of hexacoppersilsesquioxanes 1–9 containing 2,2'-bipyridine ligands. Color code: Si, yellow; O, red; C, black; H, gray; Cu, green; N, blue.

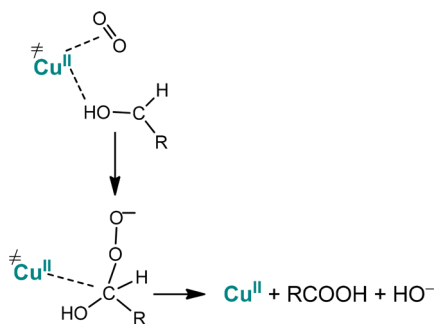


Figure 2. Presumable scheme of oxidation of a primary alcohol directly to the corresponding carboxylic acid.

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 (CDCl₃ 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. ¹³C NMR spectra were recorded on a Bruker Avance AM 100 MHz spectrometer. Chemical shifts are reported in ppm and referenced to the solvent peak (CDCl₃ at 77.16 ppm).

General Procedure for the Formation of Amides. In a sealed tube were added successively amine hydrochloride (0.5 mmol), CaCO₃ (50.1 mg, 0.5 mmol), CH₃CN (1 mL), **1** (20 μL of a solution of 1.8 mg of **1** in 2 mL of CH₂Cl₂) or **10** (40 μL of a solution of 1.7 mg of **10** in 4 mL of CHCl₃), 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 NaHCO₃ and brine and concentrated under reduced pressure. To remove the excess of benzylic alcohol, 80 mL of H₂O 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 ^1H 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 \times 0.2 μm \times 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 earlier³⁴ 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 $\text{PhSi}(\text{OMe})_3$ 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

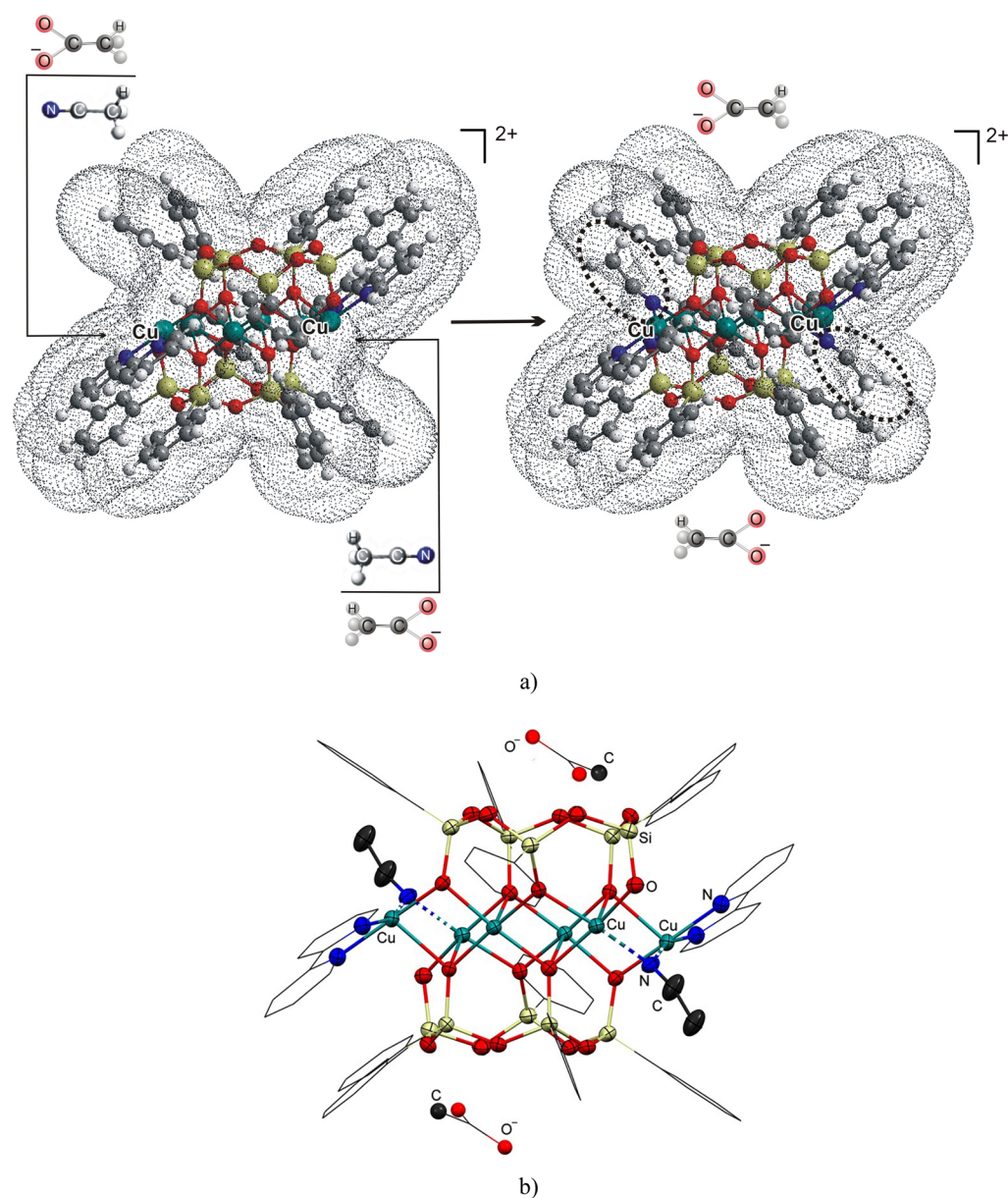


Figure 3. “Acetonitrile to copper” coordination in complex **9**: (a) van der Waals radii given to show the steric limitations; (b) molecular structure of complex **9**. Color code: Si, yellow; O, red; C, dark gray; H, light gray; Cu, green; N, blue.

metallsilsesquioxane 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 siloxanolate 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 $[(\text{PhSiO}_{1.5})(\text{NaO}_{0.5})]_n$ 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

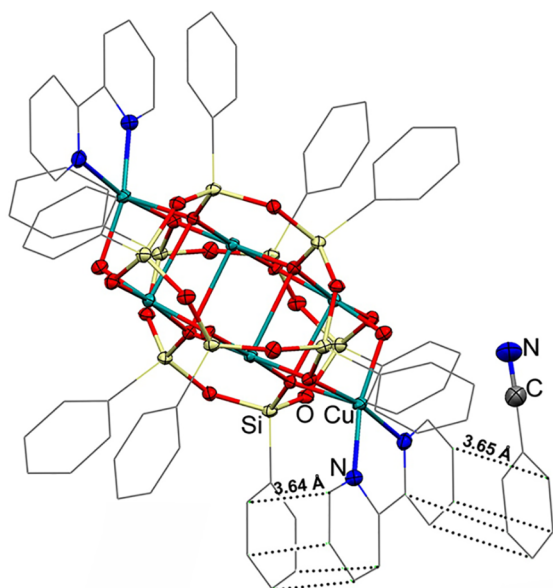


Figure 4. Triple π - π aromatic stacking (phenyl group–bipy–benzonitrile) interactions in complex **5**. Color code: Si, yellow; O, red; C, gray; Cu, green; N, blue.

hexacopper complexes **1–9** (Figure 1). These products are characterized by the presence of analogous central frameworks, with two cisoid silsesquioxane rings $[(\text{PhSiO}_{1.5})_5]$ forming a skewed sandwich cage.

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

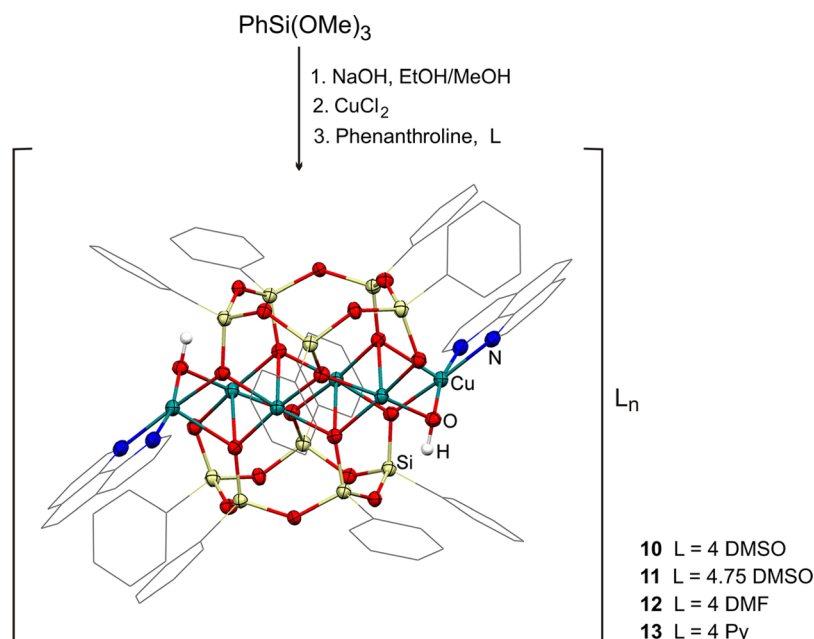


Figure 5. General scheme of synthesis of hexacoppersilsesquioxanes **10–13** containing 1,10-phenanthroline ligands. Color code: Si, yellow; O, red; H, white; Cu, green; N, blue.

to observe a specific “triple π - π 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

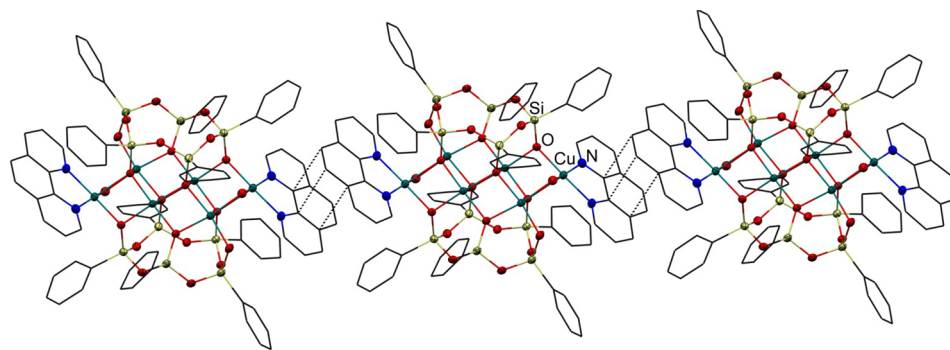


Figure 6. π - π aromatic stacking (“phenanthroline to phenanthroline”) in complex 11. Color code: Si, yellow; O, red; Cu, green; N, blue.

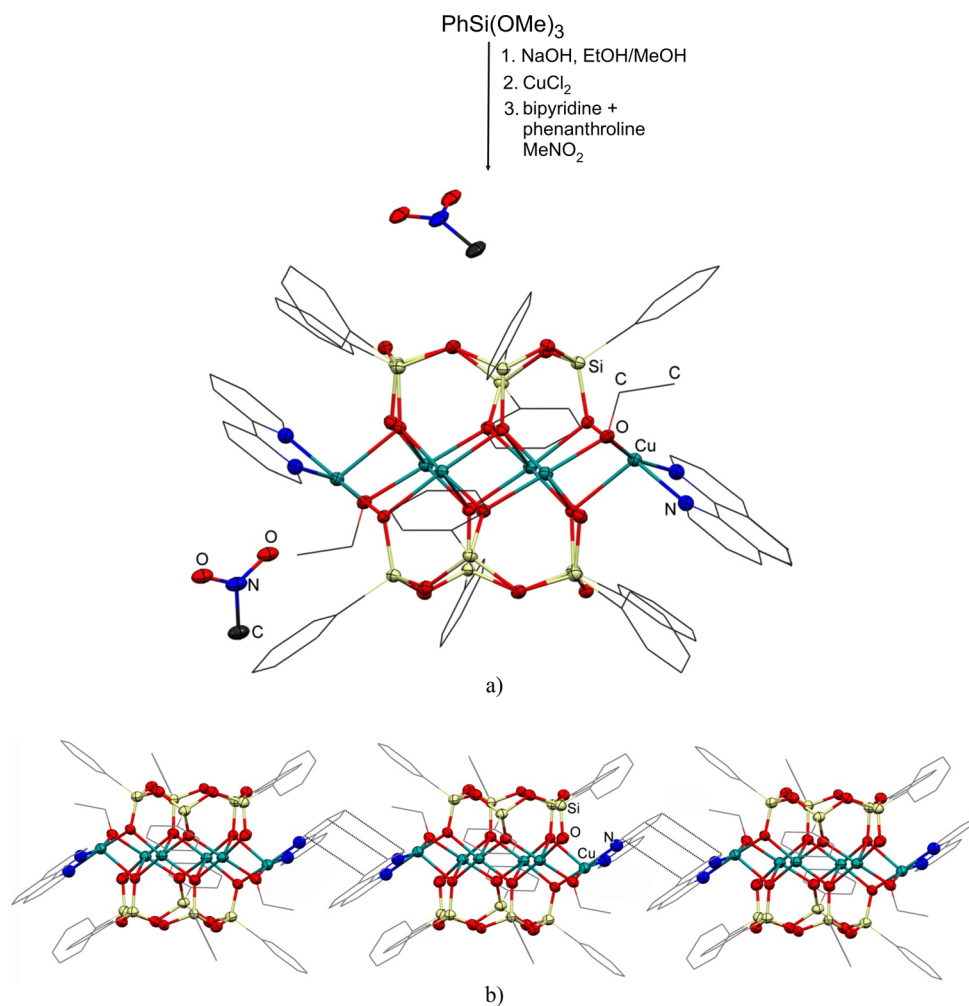


Figure 7. (a) General scheme of synthesis of hexacoppersilsesquioxane containing 1,10-phenanthroline and 2,2'-bipyridine ligands 14. (b) π - π aromatic stacking (“phenanthroline to bipyridine”) in complex 14. Color code: Si, yellow; O, red; C, black; Cu, green; N, blue.

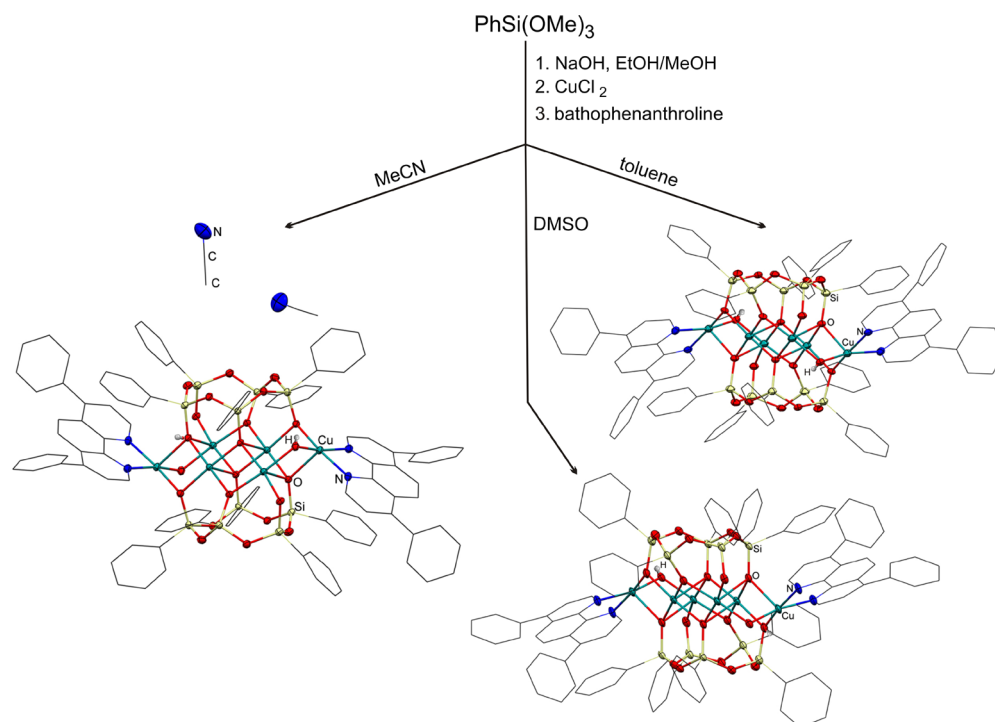


Figure 8. General scheme of synthesis of hexacoppersilsesquioxanes 15–17 containing bathophenanthroline ligands. Color code: Si, yellow; O, red; C, black; Cu, green; N, blue.

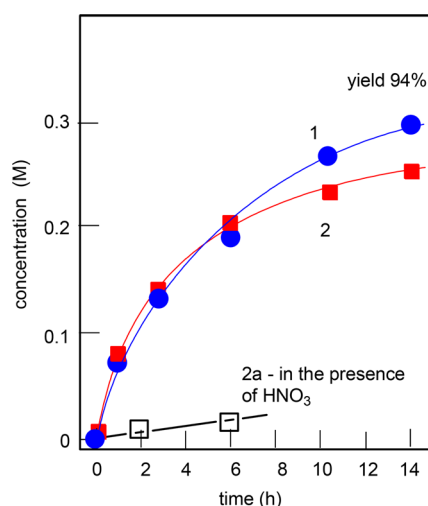


Figure 9. Accumulation of acetophenone with time in the oxidation of 1-phenylethanol (initial concentration was 0.33 M) with TBHP (70% aqueous; initial concentration 1.2 M) catalyzed by compounds **10** (5×10^{-4} M, curve 1) and **1** (5×10^{-4} M, curve 2; curve 2a, in the presence of 0.05 M of HNO_3).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

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

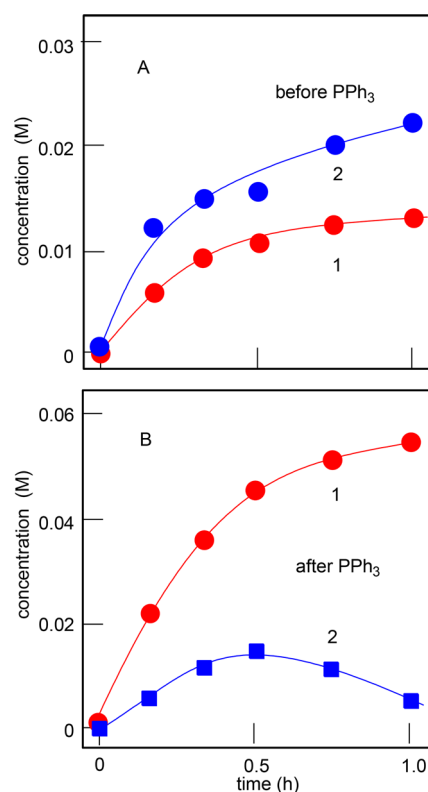


Figure 10. Oxidation of cyclohexane (0.46 M) with H_2O_2 (50%, 3 M) catalyzed by complex **10** (5×10^{-4} M) in the presence of HNO_3 (0.05 M) at 60 °C. Concentrations of cyclohexanol (curves 1) and cyclohexanone (curves 2) were measured both before and after reduction with PPh_3 .

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 by 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” CH₃COO⁻ 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 ($\angle\text{ONO} = 125.9^\circ$, $\angle\text{OCO} = 129.2^\circ$). 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 Si₁₀Cu₆ 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, Me₈Si₈Cu₃, 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 H₂O₂. Thus, the reaction of benzene (0.3 M) with H₂O₂ (50%, 3 M) in the presence of **10** (5 × 10⁻⁴ M) and HNO₃ (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 H₂O₂ 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 PPh₃ to the corresponding alcohol. The chromatogram obtained after reduction with PPh₃ 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 H₂O₂ occurs without retention of configuration (the *trans/cis* ratio was

Table 1. Regioselectivity Parameters in the *n*-Heptane (0.46 M) Oxidation with H₂O₂ (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

^aThe 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

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

^aReaction conditions: amine·HCl (0.5 mmol), benzyl alcohol (1.0 mmol), CaCO₃ (99.995% pure; 0.5 mmol), TBHP (5.5 M in nonane, 2.5 mmol), **1** or **10** (100 ppm of Cu), CH₃CN (1 mL), 80 °C, 24 h. Isolated yields are given. ^bTON = (mmol of product)/(mmol of Cu). ^cTOF = TON/(reaction time); given in h⁻¹.

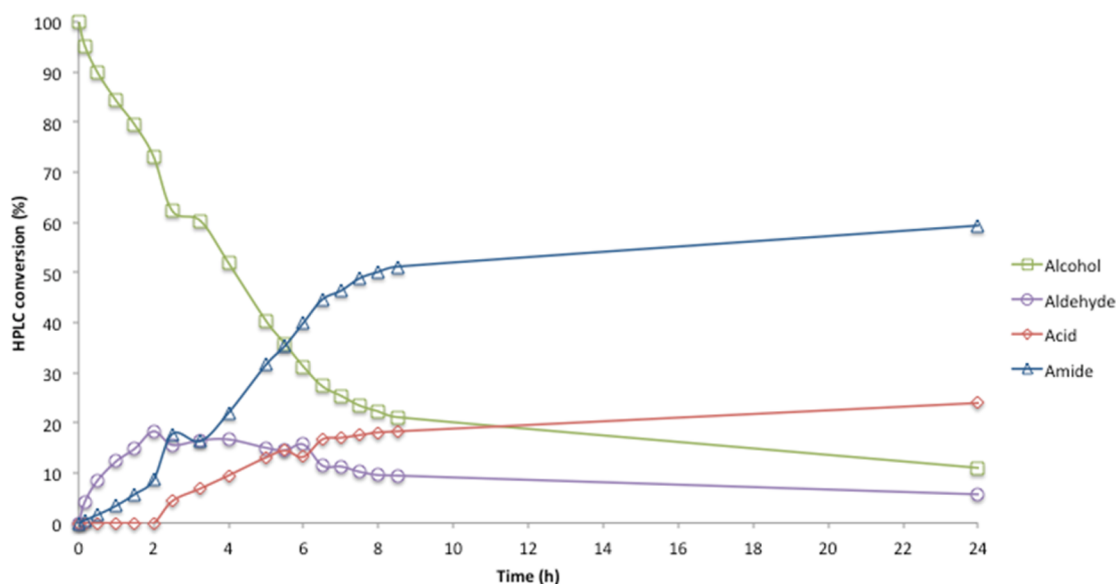
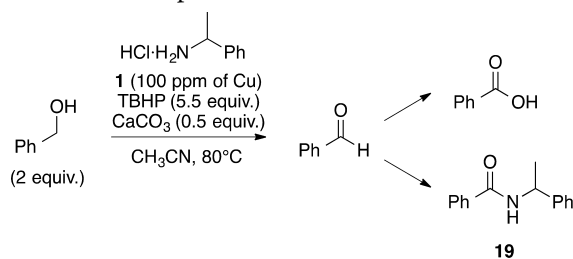


Figure 11. Conversion of benzylic alcohol in the oxidative amidation reaction.

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 H₂O₂ 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 ruthenium⁴⁴ 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:



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 cage-like 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 batho-phenanthroline (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 (Si₁₀Cu₆) 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 H₂O₂ 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.

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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REFERENCES

(1) (a) Tranchemontagne, D. J.; Ni, Z.; O’Keeffe, M.; Yaghi, O. M. Reticular chemistry of metal-organic polyhedra. *Angew. Chem., Int. Ed.* **2008**, *47*, 5136–5147. (b) Dalgarno, S. J.; Power, N. P.; Atwood, J. L. Metallo-supramolecular capsules. *Coord. Chem. Rev.* **2008**, *252*, 825–841. (c) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. Supramolecular Coordination: Self-Assembly of Finite Two- and Three-Dimensional Ensembles. *Chem. Rev.* **2011**, *111*, 6810–6918. (d) Smulders, M. M. J.; Riddell, I. A.; Browne, C.; Nitschke, J. R. Building on architectural

principles for three-dimensional metallocsupramolecular construction. *Chem. Soc. Rev.* **2013**, *42*, 1728–1754. (e) Ahmad, N.; Chughtai, A. H.; Younus, H. A.; Verpoort, F. Discrete metal-carboxylate self-assembled cages: Design, synthesis and applications. *Coord. Chem. Rev.* **2014**, *280*, 1–27.

(2) (a) Koblenz, T. S.; Wassenaar, J.; Reek, J. N. H. Reactivity within a confined self-assembled nanospace. *Chem. Soc. Rev.* **2008**, *37*, 247–262. (b) Miras, H. N.; Yan, J.; Long, D.-L.; Cronin, L. Engineering polyoxometalates with emergent properties. *Chem. Soc. Rev.* **2012**, *41*, 7403–7430. (c) Balch, A. L. Editorial for the Virtual Issue on Inorganic Cages and Containers. *Inorg. Chem.* **2014**, *53*, 3921–3925. (d) Vardhan, H.; Yusubov, M.; Verpoort, F. Self-assembled metal–organic polyhedra: An overview of various applications. *Coord. Chem. Rev.* **2016**, *306*, 171–194.

(3) (a) Foster, J. A.; Parker, R. M.; Belenguer, A. M.; Kishi, N.; Sutton, S.; Abell, C.; Nitschke, J. R. Differentially Addressable Cavities within Metal–Organic Cage-Cross-Linked Polymeric Hydrogels. *J. Am. Chem. Soc.* **2015**, *137*, 9722–9729. (b) Zhukhovitskiy, A. V.; Zhong, M.; Keeler, E. G.; Michaelis, V. K.; Sun, J. E. P.; Hore, M. J. A.; Pochan, D. J.; Griffin, R. G.; Willard, A. P.; Johnson, J. A. Highly branched and loop-rich gels via formation of metal–organic cages linked by polymers. *Nat. Chem.* **2015**, *8*, 33–41. (c) Hosono, N.; Gochomori, M.; Matsuda, R.; Sato, H.; Kitagawa, S. Metal–Organic Polyhedral Core as a Versatile Scaffold for Divergent and Convergent Star Polymer Synthesis. *J. Am. Chem. Soc.* **2016**, *138*, 6525–6531.

(4) (a) Therrien, B. Drug Delivery by Water-Soluble Organometallic Cages. *Top. Curr. Chem.* **2011**, *319*, 35–56. (b) McNeill, S. M.; Preston, D.; Lewis, J. E. M.; Robert, A.; Knerr-Rupp, K.; Graham, D. O.; Wright, J. R.; Giles, G. I.; Crowley, J. D. Biologically active [Pd₂L₄]⁴⁺ quadruply-stranded helicates: stability and cytotoxicity. *Dalton Trans.* **2015**, *44*, 11129–11136. (c) Ahmedova, A.; Mihaylova, R.; Momekova, D.; Shestakova, P.; Stoykova, S.; Zaharieva, J.; Yamashina, M.; Momekov, G.; Akitad, M.; Yoshizawa, M. M₂L₄ coordination capsules with tunable anticancer activity upon guest encapsulation. *Dalton Trans.* **2016**, *45*, 13214–13221. (d) Han, J.; Schmidt, A.; Zhang, T.; Permentier, H.; Groothuis, G. M. M.; Bischoff, R.; Kühn, F. E.; Horvatovich, P.; Casini, A. Bioconjugation strategies to couple supramolecular exo-functionalized palladium cages to peptides for biomedical applications. *Chem. Commun.* **2017**, *53*, 1405–1408.

(5) (a) Ward, M. D.; Raithby, P. R. Functional behaviour from controlled self-assembly: challenges and prospects. *Chem. Soc. Rev.* **2013**, *42*, 1619–1636. (b) Lu, W.; Wei, Z.; Gu, Z.-Y.; Liu, T.-F.; Park, J.; Park, J.; Tian, J.; Zhang, M.; Zhang, Q.; Gentle, T., III; Bosch, M.; Zhou, H.-C. Tuning the structure and function of metal–organic frameworks via linker design. *Chem. Soc. Rev.* **2014**, *43*, 5561–5593. (c) Holloway, L. R.; Young, M. C.; Beran, G. J. O.; Hooley, R. J. High fidelity sorting of remarkably similar components via metal-mediated assembly. *Chem. Sci.* **2015**, *6*, 4801–4806. (d) Jansze, S. M.; Cecot, G.; Wise, M. D.; Zhurov, K. O.; Ronson, T. K.; Castilla, A. M.; Finelli, A.; Pattison, P.; Solari, E.; Scopelliti, R.; Zelinskii, G. E.; Vologzhanina, A. V.; Voloshin, Y. Z.; Nitschke, J. R.; Severin, K. Ligand Aspect Ratio as a Decisive Factor for the Self-Assembly of Coordination Cages. *J. Am. Chem. Soc.* **2016**, *138*, 2046–2054. (e) Metherell, A. J.; Ward, M. D. Imposing control on self-assembly: rational design and synthesis of a mixed-metal, mixed-ligand coordination cage containing four types of component. *Chem. Sci.* **2016**, *7*, 910–915.

(6) (a) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. Hetero- and Metallasiloxanes Derived from Silanediols, Disilanol, Silanetriols, and Trisilanol. *Chem. Rev.* **1996**, *96*, 2205–2236. (b) Lorenz, V.; Fischer, A.; Gießmann, S.; Gilje, J. W.; Gun’ko, Y.; Jacob, K.; Edelmann, F. T. Disiloxanediolates and polyhedral metallasilsesquioxanes of the early transition metals and f-elements. *Coord. Chem. Rev.* **2000**, *206–207*, 321–368. (c) Roesky, H. W.; Anantharaman, G.; Chandrasekhar, V.; Jancik, V.; Singh, S. Control of Molecular Topology and Metal Nuclearity in Multimetallic Assemblies: Designer Metallasiloxanes Derived from Silanetriols. *Chem. - Eur. J.* **2004**, *10*, 4106–4114. (d) Lorenz, V.; Edelmann, F. T. Metallasilsesquioxanes. *Adv. Organomet. Chem.* **2005**, *53*, 101–153. (e) Edelmann, F. T. Metallasilsesquioxanes. Synthetic and Structural

- Studies. In *Silicon Chemistry: From the Atom to Extended Systems*; Jutz, P., Schubert, U., Eds.; Wiley: Hoboken, NJ, 2007; pp 383–394.
- (f) Levitsky, M. M.; Bilyachenko, A. N. Modern concepts and methods in the chemistry of polyhedral metallasiloxanes. *Coord. Chem. Rev.* **2016**, *306*, 235–269. (g) Hirotsu, M.; Taruno, S.; Yoshimura, T.; Ueno, K.; Unno, M.; Matsumoto, H. *Chem. Lett.* **2005**, *34*, 1542–1543. (h) Chandrasekhar, V.; Thirumoorthi, R. Tellurasiloxane Cages Containing Te6Si4O12 and Te6Si6O15 Frameworks. *Inorg. Chem.* **2009**, *48*, 6236–6241. (i) Ehle, S.; Lorenz, V.; Liebing, P.; Hilfert, L.; Edelmann, F. T. Synthesis and structural characterization of two complex tantalum(V) siloxides. *Inorg. Chem. Commun.* **2016**, *74*, 82–85. (j) Prabhu, M. S. R.; Ugandhar, U.; Baskar, V. In situ generated polysiloxanes stabilizing μ 3-oxo bridged Sb3 triangles. *Dalton Trans.* **2016**, *45*, 6963–6967. (k) Lokare, K. S.; Frank, N.; Braun-Cula, B.; Goikoetxea, I.; Sauer, J.; Limberg, C. Trapping Aluminum Hydroxide Clusters with Trisilanols during Speciation in Aluminum(III)–Water Systems: Reproducible, Large Scale Access to Molecular Aluminate Models. *Angew. Chem., Int. Ed.* **2016**, *55*, 12325–12329. (l) Gießmann, S.; Lorenz, V.; Liebing, P.; Hilfert, L.; Fischer, A.; Edelmann, F. T. Synthesis and structural study of new metallasilsesquioxanes of potassium and uranium. *Dalton Trans.* **2017**, *46*, 2415–2419. (m) Manicke, N.; Hoof, S.; Keck, M.; Braun-Cula, B.; Feist, M.; Limberg, C. A Hexanuclear Iron(II) Layer with Two Square-Planar FeO₄ Units Spanned by Tetrasiloxane Ligands: Mimicking of Minerals and Catalysts. *Inorg. Chem.* **2017**, *56*, 8554–8561.
- (7) (a) Bilyachenko, A. N.; Yalymov, A. I.; Korlyukov, A. A.; Long, J.; Larionova, J.; Guari, Y.; Zubavichus, Y. V.; Trigub, A. L.; Shubina, E. S.; Eremenko, I. L.; Efimov, N. N.; Levitsky, M. M. Heterometallic Na₆Co₃ Phenylsilsesquioxane Exhibiting Slow Dynamic Behavior in its Magnetization. *Chem. - Eur. J.* **2015**, *21*, 18563–18565. (b) Bilyachenko, A. N.; Yalymov, A. I.; Korlyukov, A. A.; Long, J.; Larionova, J.; Guari, Y.; Vologzhanina, A. V.; Es'kova, M. A.; Shubina, E. S.; Levitsky, M. M. Unusual penta- and hexanuclear Ni(II)-based silsesquioxane polynuclear complexes. *Dalton Trans.* **2016**, *45*, 7320–7327. (c) Bilyachenko, A. N.; Levitsky, M. M.; Yalymov, A. I.; Korlyukov, A. A.; Vologzhanina, A. V.; Kozlov, Yu. N.; Shul'pina, L. S.; Nesterov, D. N.; Pompeiro, A. J. L.; Lamaty, F.; Bantreil, X.; Fetre, A.; Liu, D.; Martinez, Long, J.; Larionova, J.; Guari, Y.; Trigub, A. L.; Zubavichus, Y. V.; Golub, I. E.; Filippov, O. A.; Shubina, E. S.; Shul'pin, G. B. A heterometallic (Fe₆Na₈) cage-like silsesquioxane: synthesis, structure, spin glass behavior and high catalytic activity. *RSC Adv.* **2016**, *6*, 48165–48180. (d) Bilyachenko, A. N.; Yalymov, A. I.; Levitsky, M. M.; Korlyukov, A. A.; Eskova, M. A.; Long, J.; Larionova, J.; Guari, Y.; Shul'pina, L. S.; Ikonnikov, N. S.; Trigub, A. L.; Zubavichus, Y. V.; Golub, I. E.; Shubina, E. S.; Shul'pin, G. B. First Cage-Like Pentanuclear Co(II)-Silsesquioxane. *Dalton Trans.* **2016**, *45*, 13663–13666.
- (8) (a) Maxim, N.; Overweg, A.; Kooyman, P. J.; van Wolput, J. H. M. C.; Hanssen, R. W. J. M.; van Santen, R. A.; Abbenhuis, H. C. L. Synthesis and Characterization of Microporous Fe–Si–O Materials with Tailored Iron Content from Silsesquioxane Precursors. *J. Phys. Chem. B* **2002**, *106*, 2203–2209 and references cited therein. (b) Murugavel, R.; Davis, P.; Shete, V. S. Reactivity Studies, Structural Characterization, and Thermolysis of Cubic Titanosiloxanes: Precursors to Titanosilicate Materials Which Catalyze Olefin Epoxidation. *Inorg. Chem.* **2003**, *42*, 4696–4706. (c) Beletskiy, E. V.; Hou, X.; Shen, Z.; Gallagher, J. R.; Miller, J. T.; Wu, Y.; Li, T.; Kung, M. C.; Kung, H. H. Supported Tetrahedral Oxo-Sn Catalyst: Single Site, Two Modes of Catalysis. *J. Am. Chem. Soc.* **2016**, *138*, 4294–4297.
- (9) Davies, G.-L.; O'Brien, J.; Gun'ko, Y. K. Rare Earth Doped Silica Nanoparticles via Thermolysis of a Single Source Metallasilsesquioxane Precursor. *Sci. Rep.* **2017**, *7*, 45862.
- (10) (a) Hanssen, R. W. J. M.; van Santen, R. A.; Abbenhuis, H. C. L. The Dynamic Status Quo of Polyhedral Silsesquioxane Coordination Chemistry. *Eur. J. Inorg. Chem.* **2004**, *2004*, 675–683. (b) Quadrelli, E. A.; Basset, J.-M. On silsesquioxanes' accuracy as molecular models for silica-grafted complexes in heterogeneous catalysis. *Coord. Chem. Rev.* **2010**, *254*, 707–728. (c) Ward, A. J.; Masters, A. F.; Maschmeyer, T. Metallasilsesquioxanes: Molecular Analogues of Heterogeneous Catalysts. *Adv. Silicon Sci.* **2011**, *3*, 135–166. (d) Levitsky, M. M.; Yalymov, A. I.; Kulakova, A. N.; Petrov, A. A.; Bilyachenko, A. N. Cage-like metallasilsesquioxanes in catalysis: A review. *J. Mol. Catal. A: Chem.* **2017**, *426*, 297–304.
- (11) (a) Duchateau, R. Incompletely Condensed Silsesquioxanes: Versatile Tools in Developing Silica-Supported Olefin Polymerization Catalysts. *Chem. Rev.* **2002**, *102*, 3525–3542 and references cited therein. (b) Wu, G.; Chen, Y.; Xu, D.-J.; Liu, J.-C.; Sun, W.; Shen, Z. Synthesis and molecular structure of a tetrameric neodymium-silsesquioxane cage complex: {[i-C₄H₉]₇(Si₇O₁₂) Nd]₄NaCl}. *J. Organomet. Chem.* **2009**, *694*, 1571–1574. (c) Varga, V.; Pinkas, J.; Gyepes, R.; Štěpnička, P.; Horáček, M.; Bastl, Z.; Mach, K. Synthesis of zirconocene silsesquioxane complexes and their ethene polymerization activity in systems with methylaluminoxane. *Collect. Czech. Chem. Commun.* **2010**, *75*, 105–119. (d) Białek, M.; Pochwała, M.; Franczyk, A.; Czaja, K.; Marciniak, B. Synthesis and catalytic properties for olefin polymerization of new vanadium complexes containing silsesquioxane ligands with different denticity. *Polym. Int.* **2017**, *66*, 960–967.
- (12) (a) Di Iulio, C.; Jones, M. D.; Mahon, M. F.; Apperley, D. C. Zinc(II) Silsesquioxane Complexes and Their Application for the Ring-Opening Polymerization of rac-Lactide. *Inorg. Chem.* **2010**, *49*, 10232–10234. (b) Monticelli, O.; Cavallo, D.; Bocchini, S.; Frache, A.; Carniato, F.; Tonelotto, A. A novel use of Ti-POSS as initiator of L-lactide ring-opening polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 4794–4799. (c) Di Iulio, C.; Jones, M. D.; Mahon, M. F. Synthesis of Al(III) silsesquioxane complexes and their exploitation for the ring opening polymerisation of rac-lactide. *J. Organomet. Chem.* **2012**, *718*, 96–100.
- (13) (a) Abbenhuis, H. C. L. Advances in Homogeneous and Heterogeneous Catalysis with Metal-Containing Silsesquioxanes. *Chem. - Eur. J.* **2000**, *6*, 25–32. (b) Pescarmona, P. P.; van der Waal, J. C.; Maxwell, I. E.; Maschmeyer, T. A New, Efficient Route to Titanium-Silsesquioxane Epoxidation Catalysts Developed by Using High-Speed Experimentation Techniques. *Angew. Chem., Int. Ed.* **2001**, *40*, 740–743. (c) Ventura, M.; Taberner, V.; Cuenca, T.; Royo, B.; Jiménez, G. *Eur. J. Inorg. Chem.* **2016**, *2016*, 2843–2849. (d) Guillo, P.; Lipschutz, M. I.; Fasulo, M. E.; Tilley, T. D. Tantalum–polyhedral oligosilsesquioxane (POSS) complexes as structural models and functional catalysts for epoxidation. *ACS Catal.* **2017**, *7*, 2303.
- (14) Duchateau, R.; van Meerendonk, W. J.; Huijser, S.; Staal, B. B. P.; van Schilt, M. A.; Gerritsen, G.; Meetsma, A.; Koning, C. E.; Kemmere, M. F.; Keurentjes, J. T. F. *Organometallics* **2007**, *26*, 4204–4211.
- (15) Beletskiy, E. V.; Shen, Z.; Rioski, M. V.; Hou, X.; Gallagher, J. R.; Miller, J. T.; Wu, Y.; Kung, H. H.; Kung, M. C. Tetrahedral Sn–silsesquioxane: synthesis, characterization and catalysis. *Chem. Commun.* **2014**, *50*, 15699–15701.
- (16) Ritter, U.; Winkhofer, N.; Murugavel, R.; Voigt, A.; Stalke, D.; Roesky, H. W. *J. Am. Chem. Soc.* **1996**, *118*, 8580–8587.
- (17) (a) Shul'pin, G. B. New Trends in Oxidative Functionalization of Carbon–Hydrogen Bonds: A Review. *Catalysts* **2016**, *6*, 50. (b) Levitsky, M. M.; Bilyachenko, A. N.; Shul'pin, G. B. Oxidation of C–H compounds with peroxides catalyzed by polynuclear transition metal complexes in Si- or Ge-silsesquioxane frameworks. *J. Organomet. Chem.* **2017**, *849–850*, 201. (c) Bilyachenko, A. N.; Kulakova, A. N.; Shul'pina, L. S.; Levitsky, M. M.; Korlyukov, A. A.; Khrustalev, V. N.; Zubavichus, Y. V.; Dorovatovskii, P. V.; Tsareva, U. S.; Shubina, E. S.; Petrov, A. A.; Vorontsov, N. V.; Shul'pin, G. B. A Family of Penta- and Hexanuclear Metallasilsesquioxanes: Synthesis, Structure and Catalytic Properties in Oxidations. *J. Organomet. Chem.* **2018**, DOI: [10.1016/j.jorganchem.2017.10.033](https://doi.org/10.1016/j.jorganchem.2017.10.033).
- (18) (a) Bilyachenko, A. N.; Dronova, M. S.; Yalymov, A. I.; Lamaty, F.; Bantreil, X.; Martinez, J.; Bizet, C.; Shul'pina, L. S.; Korlyukov, A. A.; Arkhipov, D. E.; Levitsky, M. M.; Shubina, E. S.; Kirillov, A. M.; Shul'pin, G. B. Cage-like Copper(II) Silsesquioxanes: Transmetalation Reactions and Structural, Quantum Chemical, and Catalytic Studies. *Chem. - Eur. J.* **2015**, *21*, 8758–8770. (b) Yalymov, A. I.; Bilyachenko, A. N.; Levitsky, M. M.; Korlyukov, A. A.; Khrustalev, V. N.; Shul'pina, L. S.; Dorovatovskii, P. V.; Es'kova, M. A.; Lamaty, F.; Bantreil, X.; VILLEMEJEANNE, B.; Martinez, J.; Shubina, E. S.; Kozlov, Y. N.; Shul'pin, G. B. High Catalytic Activity of Heterometallic (Fe₆Na₇ and Fe₆Na₆)

Cage Silsesquioxanes in Oxidations with Peroxides. *Catalysts* **2017**, *7* (4), 101.

(19) Bilyachenko, A. N.; Kulakova, A. N.; Levitsky, M. M.; Korlyukov, A. A.; Khrustalev, V. N.; Vologzhanina, A. V.; Titov, A. A.; Dorovatovskii, P. V.; Shul'pina, L. S.; Lamaty, F.; Bantrel, X.; Vilemejeanne, B.; Ruiz, C.; Martinez, J.; Shubina, E. S.; Shul'pin, G. B. Ionic Complexes of Tetra- and Nonanuclear Cage Cu(II)-phenylsilsesquioxanes: Synthesis and High Activity in Oxidative Catalysis. *ChemCatChem* **2017**, DOI: 10.1002/cctc.201701063.

(20) Feher, F. J. Polyhedral oligometallasilsesquioxanes (POMSS) as models for silica-supported transition-metal catalysts. Synthesis and characterization of $(C_5Me_5)Zr[(Si_7O_{12})(C-C_6H_{11})_7]$. *J. Am. Chem. Soc.* **1986**, *108*, 3850–3852.

(21) Fei, Z.; Busse, S.; Edelman, F. T. The first tantalasilsesquioxanes. *J. Chem. Soc., Dalton Trans.* **2002**, 2587–2589.

(22) Duchateau, R.; Dijkstra, T. W.; Severn, J. R.; van Santen, R. A.; Korobkov, I. V. Synthesis and characterization of tin containing polyhedral oligometallasilsesquioxanes (POMSS). *Dalton Trans.* **2004**, 2677–2682.

(23) Baker, R. T.; Ott, K. C.; Tumas, W.; Liu, F.; John, K. D.; Scott, B. L. Synthesis and Characterization of Iron Silsesquioxane Phosphane Complexes. *Angew. Chem., Int. Ed.* **2000**, *39*, 3127–3130.

(24) Quadrelli, E. A.; Davies, J. E.; Johnson, B. F. G.; Feeder, N. Molecular insight into the non-innocence of a silica-support: the structure of a platinum–silsesquioxane derivative. *Chem. Commun.* **2000**, 1031–1032.

(25) Voigt, A.; Walawalkar, M. G.; Murugavel, R.; Roesky, H. W.; Parisini, E.; Lubini, P. Organic-Soluble Neutral and Ionic Indium Siloxane Cages: Potential Precursors for Indium-Containing Silicates. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2203–2205.

(26) Nehete, U. N.; Anantharaman, G.; Chandrasekhar, V.; Murugavel, R.; Walawalkar, M. G.; Roesky, H. W.; Vidovic, D.; Magull, J.; Samwer, K.; Sass, B. Polyhedral Ferrous and Ferric Siloxanes. *Angew. Chem., Int. Ed.* **2004**, *43*, 3832–3835.

(27) Lindemann, H. M.; Schneider, M.; Neumann, B.; Stammeler, H.-G.; Stammeler, A.; Jutzi, P. Synthesis and Reactivity of Core-Functionalized Polyhedral Titanasiloxanes. *Organometallics* **2002**, *21*, 3009–3017.

(28) Abbati, G. L.; Caneschi, A.; Cornia, A.; Fabretti, A. C.; Pozdniakova, Y. A.; Shchegolikhina, O. I. Towards Stepwise Cluster Assembly: A Decacopper(II) Complex Obtained by Controlled Expansion of a Metallasiloxane Cage. *Angew. Chem., Int. Ed.* **2002**, *41*, 4517–4520.

(29) Pashchenko, V.; Brendel, B.; Wolf, B.; Lang, M.; Lyssenko, K.; Shchegolikhina, O.; Molodtsova, Y.; Zherlitsyna, L.; Auner, N.; Schütz, F.; Kollar, M.; Kopietz, P.; Harrison, N. *Eur. J. Inorg. Chem.* **2005**, *2005*, 4617–4625.

(30) Bilyachenko, A. N.; Kulakova, A. N.; Levitsky, M. M.; Petrov, A. A.; Korlyukov, A. A.; Shul'pina, L. S.; Khrustalev, V. N.; Dorovatovskii, P. V.; Vologzhanina, A. V.; Tsareva, U. S.; Golub, I. E.; Gulyaeva, E. S.; Shubina, E. S.; Shul'pin, G. B. Unusual tri-, hexa- and nonanuclear Cu(II) cage methylsilsesquioxanes: Synthesis, Structures and Catalytic Activity in Oxidations with Peroxides. *Inorg. Chem.* **2017**, *56*, 4093–4103.

(31) (a) Sergienko, N. V.; Korlyukov, A. A.; Arkhipov, D. E.; Novikov, V. V.; Eskova, M. A.; Zavin, B. G. Metallosiloxanes containing period 5 transition metals: synthesis and X-ray studies of three cadmium siloxanes. *Mendeleev Commun.* **2016**, *26*, 344–346. (b) Bilyachenko, A. N.; Yalymov, A. I.; Shul'pina, L. S.; Mandelli, D.; Korlyukov, A. A.; Vologzhanina, A. V.; Es'kova, M. A.; Shubina, E. S.; Levitsky, M. M.; Shul'pin, G. B. Novel Cage-Like Hexanuclear Nickel(II) Silsesquioxane. Synthesis, Structure, and Catalytic Activity in Oxidations with Peroxides. *Molecules* **2016**, *21*, 665.

(32) Zherlitsyna, L.; Auner, N.; Bolte, M. Bis(μ -6-cis-2,4,6,8,10,12,14,16-octamethylcycloocta-siloxane-2,4,6,8,10,12,14,16-octolato)octakis[(dimethyl-formamide)copper(II)] dimethylformamide solvate enclosing a pyrazine molecule. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2006**, *62*, m199–m200.

(33) (a) Evans, P. R. Scaling and assessment of data quality. *Acta Crystallogr., Sect. D: Biol. Crystallogr.* **2006**, *62*, 72–82. (b) Batty, T. G. G.; Kontogiannis, L.; Johnson, O.; Powell, H. R.; Leslie, A. G. W. *iMOSFLM*: a new graphical interface for diffraction-image processing with *MOSFLM*. *Acta Crystallogr., Sect. D: Biol. Crystallogr.* **2011**, *67*, 271–281. (c) Sheldrick, G. M. *SADABS*, v. 2.03, Bruker/Siemens Area Detector Absorption Correction Program; Bruker AXS Inc., Madison, WI, 2003. (d) *SAINT*, v. 8.27A; Bruker AXS Inc., Madison, WI, 2012. (e) Spek, A. L. *PLATON*, A Multipurpose Crystallographic Tool; Utrecht University, Utrecht, The Netherlands, 2006. (f) Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71*, 3–8. (g) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

(34) (a) Shul'pin, G. B.; Druzhinina, A. N. Hydroperoxidation of alkanes by atmospheric oxygen in the presence of hydroquinone or quinone catalyzed by copper(II) acetate under visible light irradiation. *React. Kinet. Catal. Lett.* **1992**, *47*, 207–211. (b) Shul'pin, G. B. Metal-catalyzed hydrocarbon oxygenations in solutions: the dramatic role of additives: a review. *J. Mol. Catal. A: Chem.* **2002**, *189*, 39–66. (c) Shul'pin, G. B. Metal-catalysed hydrocarbon oxidations. *C. R. Chim.* **2003**, *6*, 163–178. (d) Shul'pin, G. B. Hydrocarbon Oxygenations with Peroxides Catalyzed by Metal Compounds. *Mini-Rev. Org. Chem.* **2009**, *6*, 95–104. (e) Shul'pin, G. B.; Kozlov, Y. N.; Shul'pina, L. S.; Kudinov, A. R.; Mandelli, D. Extremely Efficient Alkane Oxidation by a New Catalytic Reagent $H_2O_2/Os_3(CO)_{12}/Pyridine$. *Inorg. Chem.* **2009**, *48*, 10480–10482. (f) Shul'pin, G. B.; Kozlov, Y. N.; Shul'pina, L. S.; Petrovskiy, P. V. Oxidation of alkanes and alcohols with hydrogen peroxide catalyzed by complex $Os_3(CO)_{10}(\mu-H)_2$. *Appl. Organomet. Chem.* **2010**, *24*, 464–472. (g) Shul'pin, G. B. Selectivity enhancement in functionalization of C–H bonds: A review. *Org. Biomol. Chem.* **2010**, *8*, 4217–4228. (h) Shul'pin, G. B. New Trends in Oxidative Functionalization of Carbon–Hydrogen Bonds: A Review. *Catalysts* **2016**, *6*, 50. (i) Olivo, G.; Lanzalunga, O.; Di Stefano, S. Non-Heme Imine-Based Iron Complexes as Catalysts for Oxidative Processes. *Adv. Synth. Catal.* **2016**, *358*, 843–863. (j) Garcia-Bosch, I.; Siegel, M. A. Copper-Catalyzed Oxidation of Alkanes with H_2O_2 under a Fenton-like Regime. *Angew. Chem.* **2016**, *128*, 13065–13068.

(35) (a) Dubchak, I. L.; Shklover, V. E.; Levitsky, M. M.; Zhdanov, A. A.; Struchkov, Y. T. Crystal structure of siloxanes and silazanes. *J. Struct. Chem.* **1981**, *21*, 778–786. (b) Schmidt-Bäse, D.; Klingebiel, U. Lithium-Verbindungen eines Silandiols, 1-Fluor-1,3-disiloxan-3-ols und 1-Fluor-1,3,5-trisiloxan-5-ols; Synthese und Kristallstrukturen. *Chem. Ber.* **1989**, *122*, 815–821. (c) Hursthouse, M. B.; Hossain, M. A.; Motevalli, M.; Sanganee, M.; Sullivan, A. C. Synthesis and structure of the unusual dimeric lithium derivative of the tetraphenyldisiloxanediolate dianion. *J. Organomet. Chem.* **1990**, *381*, 293–297. (d) Schütte, S.; Klingebiel, U.; Schmidt-Bäse, D. Alkalisilanolate und -siloxanolate als Precursor für Si–O-Ringe. *Z. Naturforsch., B: J. Chem. Sci.* **1993**, *48*, 263–269. (e) Motevalli, M.; Shah, D.; Sullivan, A. C. Solid-state and solution structures of some lithium salts of tetraphenyldisiloxanediolate(2–) and the lithium-bridged compounds $Li_2[M-(OSiPh_2OSiPh_2O)_3-3py]$ (py = pyridine, M = Zr or Hf). *J. Chem. Soc., Dalton Trans.* **1993**, 2849–2855. (f) Lickiss, P. D. The Synthesis and Structures of Organosilanols. *Adv. Inorg. Chem.* **1995**, *42*, 147–262. (g) Feher, F. J.; Budzichowski, T. A. Silsesquioxanes as ligands in inorganic and organometallic chemistry. *Polyhedron* **1995**, *14*, 3239–3253. (h) Annand, J.; Aspinall, H. C.; Steiner, A. Novel Heterometallic Lanthanide Silsesquioxane. *Inorg. Chem.* **1999**, *38*, 3941–3943. (i) Shchegolikhina, O.; Pozdniakova, Y.; Antipin, M.; Katsoulis, D.; Auner, N.; Herrschaft, B. Synthesis and Structure of Sodium Phenylsiloxanolate. *Organometallics* **2000**, *19*, 1077–1082. (j) Lorenz, V.; Gießmann, S.; Gun'ko, Y. K. Fully Metalated Silsesquioxanes: Building Blocks for the Construction of Catalyst Models. *Angew. Chem., Int. Ed.* **2004**, *43*, 4603–4606. (k) Pozdniakova, Y. A.; Lyssenko, K. A.; Korlyukov, A. A.; Blagodatskikh, I. V.; Auner, N.; Katsoulis, D.; Shchegolikhina, O. I. Alkali-Metal-Directed Hydrolytic Condensation of Trifunctional Phenylalkoxysilanes. *Eur. J. Inorg. Chem.* **2004**, *2004*,

- 1253–1261. (l) Pozdnyakova, Yu. A.; Chetverikov, A. A.; Lyssenko, K. A.; Peregodov, A. S.; Buzin, M. I.; Matukhina, E. V.; Shchegolikhina, O. I. Synthesis, structure, and properties of sodium cis-tetraethylcyclotetrasiloxanolate and new mesomorphic cis-tetra[ethyl(trimethylsilyloxy)]-cyclotetrasiloxane. *Russ. Chem. Bull.* **2007**, *56*, 77–82. (m) Bilyachenko, A. N.; Dronova, M. S.; Yalymov, A. I.; Korlyukov, A. A.; Shul'pina, L. S.; Arkhipov, D. E.; Shubina, E. S.; Levitsky, M. M.; Kirilin, A. D.; Shul'pin, G. B. Binuclear Cage-Like Copper(II) Silsesquioxane ("Cooling Tower") – Its High Catalytic Activity in the Oxidation of Benzene and Alcohols. *Eur. J. Inorg. Chem.* **2013**, *2013*, 5240–5246. (n) Pozdnyakova, Y. A.; Korlyukov, A. A.; Lyssenko, K. A.; Zherlitsyna, L.; Auner, N.; Shchegolikhina, O. I. Alkali metal organocyclotrisiloxanates [RSi(O)OM]₃ with vinyl and alkyl substituents at the silicon center. *J. Organomet. Chem.* **2013**, *729*, 86–94. (o) Čas, D.; Hurkes, N.; Spirk, S.; Belaj, F.; Bruhn, C.; Rechberger, G. N.; Pietschnig, R. Dimer formation upon deprotonation: synthesis and structure of a m-terphenyl substituted (R,S)-dilithium disiloxanolate disilanol. *Dalton Trans.* **2015**, *44*, 12818–12823. (p) Nowacka, M.; Kowalewska, A.; Gadzinowska, K. Alkali-Metal-Directed Hydrolytic Condensation of 3-Mercaptopropyltrimethoxysilane. *Silicon* **2015**, *7*, 147–153. (q) Oguri, N.; Egawa, Y.; Takeda, N.; Unno, M. Janus-Cube Octasilsesquioxane: Facile Synthesis and Structure Elucidation. *Angew. Chem., Int. Ed.* **2016**, *55*, 9336–9339. (r) Anisimov, A. A.; Zhemchugov, P. V.; Milenin, S. A.; Goloveshkin, A. S.; Tsareva, U. S.; Bushmarinov, I. S.; Korlyukov, A. A.; Takazova, R. U.; Molodtsova, Yu. A.; Muzafarova, A. M.; Shchegolikhina, O. I. Sodium cis-tetratoylcyclotetrasiloxanolate and cis-tritylcyclotrisiloxanolate: Synthesis, structure and their mutual transformations. *J. Organomet. Chem.* **2016**, *823*, 103–111. (s) Pietschnig, R.; Spirk, S. The chemistry of organo silanetriols. *Coord. Chem. Rev.* **2016**, *323*, 87–106. (t) Muzafarov, A. M. (Monosodiumoxy)-organoalkoxysilanes (Rebrov Salts)—Polyfunctional Monomers for Silicene Syntheses. In *Efficient Methods for Preparing Silicon Compounds*; Roesky, H. W., Ed.; Elsevier: Amsterdam, 2016; pp 179–181. (u) Gießmann, S.; Lorenz, V.; Liebing, P.; Hilfert, L.; Fischer, A.; Edelmann, F. T. Synthesis and structural study of new metal-silsesquioxanes of potassium and uranium. *Dalton Trans.* **2017**, *46*, 2415–2419.
- (36) (a) Tretyakov, V. P.; Zimtseva, G. P.; Rudakov, E. S.; Bogdanov, A. V. Unusual selectivity of alcohol oxidation by oxygen in aqueous alkaline solutions of copper phenanthroline complexes. *React. Kinet. Catal. Lett.* **1982**, *19*, 263–266. (b) Sakharov, A. M.; Skibida, I. P. Chemical models of enzymatic oxidation: oxidation of primary alcohols in alkaline media catalyzed by copper complexes. *J. Mol. Catal.* **1988**, *48*, 157–174.
- (37) Bilyachenko, A. N.; Korlyukov, A. A.; Vologzhanina, A. V.; Khrustalev, V. N.; Kulakova, A. N.; Long, J.; Larionova, J.; Guari, Y.; Dronova, M. S.; Tsareva, U. S.; Dorovatovskii, P. V.; Shubina, E. S.; Levitsky, M. M. Bi- and Tri-metallic Cage Silsesquioxanes: Features of Supramolecular Assembling and Magnetic Properties. *Dalton Trans.* **2017**, *46*, 12935–12949.
- (38) (a) Wójtowicz-Młochowska, H. Synthetic utility of metal catalyzed hydrogen peroxide oxidation of C-H, C-C and C=C bonds in alkanes, arenes and alkenes: Recent advances. *Arkivoc* **2017**, 12–58. (b) Anbu, S.; Paul, A.; Ribeiro, A. P. C.; da Silva, M. F. C. G.; Kuznetsov, M. L.; Pombeiro, A. J. L. Biomolecular interaction, catecholase like activity and alkane oxidation in ionic liquids of a phenylcarbohydrazone-based monocopper(II) complex. *Inorg. Chim. Acta* **2016**, *450*, 426–436. (c) Solomon, E. L.; Heppner, D. E.; Johnston, E. M.; Ginsbach, J. W.; Cirera, J.; Qayyum, M.; Kieber-Emmons, M. T.; Kjaergaard, C. H.; Hadt, R. G.; Tian, L. Copper Active Sites in Biology. *Chem. Rev.* **2014**, *114*, 3659–3853. (d) Silva, T. F. S.; Rocha, B. G. M.; da Silva, M. F. C. G.; Martins, L. M. D. R. S.; Pombeiro, A. J. L. V(IV), Fe(II), Ni(II) and Cu(II) complexes bearing 2,2,2-tris(pyrazol-1-yl)ethyl methanesulfonate: application as catalysts for the cyclooctane oxidation. *New J. Chem.* **2016**, *40*, 528–537. (e) Kirillov, A. M.; Kirillova, M. V.; Pombeiro, A. J. L. Multicopper complexes and coordination polymers for mild oxidative functionalization of alkanes. *Coord. Chem. Rev.* **2012**, *256*, 2741–2759.
- (39) (a) Shul'pin, G. B. Selectivity in C–H functionalizations. In *Comprehensive Inorganic Chemistry II*, 2nd ed.; Reedijk, J., Poepelmeier, K., Casella, L., Eds.; Elsevier: Amsterdam, 2013; Vol. 6, Chapter 6.04, pp 79–104. (b) Shul'pin, G. B. C–H functionalization: thoroughly tuning ligands at a metal ion, a chemist can greatly enhance catalyst's activity and selectivity. *Dalton Trans.* **2013**, *42*, 12794–12818.
- (40) (a) Shul'pin, G. B.; Kozlov, Y. N.; Nizova, G. V.; Süss-Fink, G.; Stanislas, S.; Kitaygorodskiy, A.; Kulikova, V. S. «Oxidations by the reagent "O₂–H₂O₂–vanadium derivative–pyrazine-2-carboxylic acid" Part 12. Main features, kinetics and mechanism of alkane hydroperoxidation». *J. Chem. Soc., Perkin Trans.* **2001**, *2*, 1351–1371. (b) Nesterov, D. S.; Chygorin, E. N.; Kokozay, V. N.; Bon, V. V.; Boča, R.; Kozlov, Y. N.; Shul'pina, L. S.; Jezierska, J.; Ozarowski, A.; Pombeiro, A. J. L.; Shul'pin, G. B. Heterometallic Co^{III}₄Fe^{III}₂ Schiff Base Complex: Structure, Electron Paramagnetic Resonance, and Alkane Oxidation Catalytic Activity. *Inorg. Chem.* **2012**, *51*, 9110–9122.
- (41) (a) Bantreil, X.; Fleith, C.; Martinez, J.; Lamaty, F. Copper-Catalyzed Direct Synthesis of Benzamides from Alcohols and Amines. *ChemCatChem* **2012**, *4*, 1922–1925. (b) Azizi, K.; Karimi, M.; Nikbakht, F.; Heydari, A. Direct oxidative amidation of benzyl alcohols using EDTA@Cu(II) functionalized superparamagnetic nanoparticles. *Appl. Catal., A* **2014**, *482*, 336–343. (c) Yedage, S. L.; Bhanage, B. M. Copper-Catalyzed Synthesis of Weinreb Amides by Oxidative Amidation of Alcohols. *Synthesis* **2015**, *47*, 526–532.
- (42) (a) Ghosh, S. C.; Ngiam, J. S. Y.; Seayad, A. M.; Tuan, D. T.; Johannes, C. W.; Chen, A. Tandem oxidative amidation of benzyl alcohols with amine hydrochloride salts catalysed by iron nitrate. *Tetrahedron Lett.* **2013**, *54*, 4922–4925. (b) Gaspa, S.; Porcheddu, A.; De Luca, L. Iron-catalysed oxidative amidation of alcohols with amines. *Org. Biomol. Chem.* **2013**, *11*, 3803–3807. (c) Bantreil, X.; Kanfar, N.; Gehin, N.; Golliard, E.; Ohlmann, P.; Martinez, J.; Lamaty, F. Iron-catalyzed benzamide formation. Application to the synthesis of moclobemide. *Tetrahedron* **2014**, *70*, 5093–5099.
- (43) Wu, X.-F.; Sharif, M.; Pews-Davtyan, A.; Langer, P.; Ayub, K.; Beller, M. The First ZnII-Catalyzed Oxidative Amidation of Benzyl Alcohols with Amines under Solvent-Free Conditions. *Eur. J. Org. Chem.* **2013**, *2013*, 2783–2787.
- (44) Gunanathan, C.; Ben-David, Y.; Milstein, D. Direct synthesis of amides from alcohols and amines with liberation of H₂. *Science* **2007**, *317*, 790–792.
- (45) (a) Zweifel, T.; Naubron, J. V.; Grutzmacher, H. Catalyzed Dehydrogenative Coupling of Primary Alcohols with Water, Methanol, or Amines. *Angew. Chem., Int. Ed.* **2009**, *48*, 559–563. (b) Fujita, K.-i.; Takahashi, Y.; Owaki, M.; Yamamoto, K.; Yamaguchi, R. Synthesis of Five-, Six-, and Seven-Membered Ring Lactams by Cp*Rh Complex-Catalyzed Oxidative N-Heterocyclization of Amino Alcohols. *Org. Lett.* **2004**, *6*, 2785–2788.