

Ionic Complexes of Tetra- and Nonanuclear Cage Cu(II)phenylsilsesquioxanes: Synthesis and High Activity in Oxidative Catalysis

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Abstract: Herein, we describe an approach to cade metallasilsesquioxanes using self-assembling reactions with participation of 1,2-bis(diphenylphosphino)ethane as a key reactant. This approach allowed us to achieve an unique family of complexes which include anionic tetra- or nonanuclear cage Cu(II),Nasilsesquioxane and cationic $\mbox{Cu(I)}\mbox{dppe}_2$ components. Additional representatives of this intriguing metallasilsesquioxane family (Cu₉Na₆ and Cu₉Na₃Cs₃) were obtained through the replacement of original ethanol-based reaction media by dmso. Fascinating structural peculiarities of all products were established by X-ray diffraction and topological studies. First tests for application of synthesized complexes as catalysts revealed their very high activity in homogeneous oxidation of alkanes and alcohols to produce alkyl hydroperoxides, ketones and amides.

Introduction

Among huge variety of 3D polycyclic (cage) metal-containing

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complexes^[1] the ones based on structural silsesquioxane (RSiO_{1.5}) fragments^[2] attract special attention as systems, perfectly simulating metal center' grafting to silica surface^[3] in heterogeneous catalytic applications.^[4] Such compounds (cagelike metallasilsesquioxanes, CLMSs) are also (i) active in homogeneous catalysis,^[5] (*ii*) demonstrate specific (spin glass) magnetic properties^[6] or (*iii*) provide opportunities of unusual reactivity^[7] and structural reorganizations, governed by thermal treatment.^[5a, 8] The most demanded synthetic approaches to CLMSs include reactions using cubane,^[9] cyclic^[10] or trisilanol^{[2,} synthones as well as self-assembling^[11b, 12] or transmetalation^[11b, 13] procedures. Here we report the preparation of new types of CLMSs, following the "double ligation principle" of self-assembling reaction. This novel way of synthesis implies the use of two types or reactants, capable to ligate metal ions in the process of cage product' assembling -O-ligand (silsesquioxane) and P-ligand (1.2 bis(diphenylphosphino)ethane, dppe). Important to differentiate this approach from several bidentate phosphine-involved syntheses of CLMSs, where phosphine served as a component of initial metal complex.^[14] Here we show prospectives of double (O-, P-) ligation approach to CLMSs, as well as tendencies of supramolecular aggregation of products and their catalytic properties in C-H compounds oxidation and amides formation.

Results and Discussion

Synthesis.

By the moment of the start of this research, several instances of the use of phenyltrialkoxysilanes as simple but efficient educts in the self-assembling of CLMSs have been reported. $^{\left[11b,12\text{-}13\right]}$ In the same time, not a single example of an involvement of the bidentate P-based ligand has been given among them. Being interested in a study of principles of double ligated (silsesquioxane/phosphine) CLMSs' formation, we have performed several parallel reactions of synthesis of Cucontaining CLMSs. Three-component mixture has been used for this self-assembling reaction: highly (i) reactive phenylsiloxanolate [(PhSiO_{1.5})(NaO_{0.5})]_n moieties (prepared in situ from PhSi(OEt)₃ and NaOH) as silsesquioxane component, (ii) 1,2-bis(diphenylphosphino)ethane as phosphine component,

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(*iii*) $CuCl_2$ as a source of transition metal ions. Among various combination of solvents used for the synthesis (including DMF, acetonitrile, THF, 1,4-dioxane,...) only ethanol was found to be a key reaction media, capable to assist the assembly of target complex (Scheme 1).



Scheme 1. Scheme of solvent variation during synthesis of Cu,Naphenylsilsesquioxanes. Use of EtOH provided 1 (in the yield of 42%) and 2 (in the yield of 17%)

It has been found that two types of compounds could be isolated this way, in dependency from the loading of NaOH (compounds 1 and 2, Figure 1). Each of products 1-2 contains CLMS fragment as an anionic component of complex, while $Cu(dppe)_2$ fragments serve as cationic fragments, balancing the electroneutrality.





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Figure 1. Molecular and ChemDraw structures of $(PhSiO_{1.5})_{12}(CuO)_4(NaO_{0.5})_2(Cu)_2(dppe)_4~1$ (solvating molecules of EtOH are omitted in the sake of clarity) and (PhSiO_{1.5})₁₂(PhSiO_{1.5})₈(CuO)₈(NaO_{0.5})₄{Cu(O_{0.5})₄}(Cu)₂(dppe)₄ 2 (solvating molecules of EtOH are omitted in the sake of clarity).

This intriguing feature of CLMS formation, to the best of our knowledge, has never been described in the chemistry of metallasilsesquioxanes. Several unusual features of both complexes deserve to be mentioned. Previously, the presence of additional organic ligands in the CLMS' formation media provoked formation of complexes where both silsesquioxane and additional ligands (e.g., triphenylphosphine oxide,^[15] ,Ν -tetramethyl-p-phenylenediamine,[16] N.N.N trimethylphosphine,^[17] tris(2-(dimethylamino)ethyl)amine,[18] pyrazine^[19]) coordinate metal ions of the same cage compound. As opposite to this "ligand synergy" situation, newly synthesized compounds 1 and 2 represent other, "ligand antagonism", principle of complexation. Namely, copper ions of both compounds 1 and 2 are redistributed between different (O- and P-) ligands, giving rise to the two-component products, where silsesquioxane O-ligands form an anionic cage fragments while phosphine P-ligands provide cationic Cu(dppe)₂ fragments. Noteworthy that composition of silsesquioxane cade components of compounds ${\bf 1}$ and ${\bf 2}$ are principally different in comparison to each other. At the first sight, cage component, observed in complex 1, is well known in the chemistry of CLMSs.^[11b, 12-13] Its sandwich-like structure is characterized by the presence of the two cyclic (PhSiO_{1.5})₆ ligands (giving negative charge of 12⁻), coordinating the Cu^{II}₄-containing core (giving positive charge of 8⁺). Note, that for all early described examples of such CLMS motives the four additional bearers of positive charge (e.g., Na⁺, Li⁺, Cs⁺ cations) were registered, and that is quite logical in sense of keeping the charge balance of the CLMS neutral. According to this logic, two sodium cations in the composition of 1 are obviously not enough to balance the negative charge (coming from silsesquioxane ligands), and the appearance of two [Cu^I(dppe)₂]⁺ fragments becomes essential to form the final complex 1 (Figure 2).



Figure 2. Coppersilsequioxane cage in 1. Color code: Si – light-yellow, O – red, Cu – blue, Na – yellow.

In turn, silsesquioxane cage component of product 2 is truly unprecedented one. First of all, nonacopper(II)silsesquioxane cage of 2 joins the very small family of nonanuclear CLMSs (the first and only known representative of that family was reported by some of us in the recent work^[20]). Anionic nonacopper cage of 2 possesses principal differences in its structure both from compound from ref. 20 as well as from all other types of CLMSs. One could observe in composition of 2 the two sandwich-like tetracopper fragments joined via central (ninth) copper ion. Such unique "fusion" structure becomes possible due to the involvement of two types of silsesquioxane ligands - two cyclyc (PhSiO_{1.5})₆ and two acyclic (PhSiO_{1.5})₄ ones. These latter are rarest types of silsesquioxane fragments, capable to coordinate metal ions of CLMSs. To the best of our knowledge, the only case of the observation of such ligand in the composition of CLMS was reported by some of us for Mn-containing silsesquioxane.^[21] Similarly to compound **1**, the negative charge, bringing by silsesquioxane matrix of compound 2, is balanced (along with Cu^{II} ions of cage component) by the four Na⁺ cations and the two [Cu¹(dppe)₂]⁺ fragments (Figure 3).



Figure 3. Coppersilsequioxane cage in 2. Color code: Si – light-yellow, O – red, Cu – blue, Na – yellow.

Being interested in further investigation of these non-trivial chemistry, we have performed some additional experiments (Scheme 2). First of all, the change of reactants ratio let us to isolate product **3**, the rare instance of compound including different (by their nuclearity) CLMSs in composition of the same complex. This product **3** involves two types of components - (*i*) compound **2** and (*ii*) hexacoppersilsesquioxane of cylinder-like structure (Figure 4).

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ChemDraw Figure Molecular structures 4 and of $\{(PhSiO_{1.5})_{12}(PhSiO_{1.5})_8(CuO)_8(NaO_{0.5})_4\{Cu(O_{0.5})_4\}\}[Cu(dppe)_2]_2[(PhSiO_{1.5})_{12}(CuO)_8(NaO_{0.5})_4]_2(CuO)_8(NaO_{0.5})_4]_2[(PhSiO_{1.5})_{12}(CuO)_8(NaO_{0.5})_4]_2[(PhSiO_{1.5})_{12}(CuO)_8(NaO_{0.5})_4]_2[(PhSiO_{1.5})_{12}(CuO)_{15})_{12}$ uO)6] 3 (solvating molecules of water and EtOH are omitted in the sake of clarity).



Then, we have tried to optimize the conditions of the synthesis of dppe-containing CLMSs. Before mentioned reactions of products 1-3 have been performed at reflux due to low solubility of dppe in ethanol at room temperature. Replacement of this reaction media by ethanol/toluene mixture (Scheme 2) allowed to reproduce synthesis of 2 at lower temperature and to isolate the analogous product 4 (Figure 5) as ethanol/toluene complex in the higher yield than compound 2 (46% vs 17%).

Scheme 2. Scheme of Cu,Na-phenylsilsesquioxane' synthesis tuning.

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Then, we have explored a suitability of other reaction systems for the isolation of structural analogues of **2**. To our surprise, the replacement of ethanol media by DMSO (Scheme 2) leads to some reorganization of structure in comparison with compound **2.** Isolated (as DMSO complex) complex **5** is similar (regarding the silsesquioxane skeleton) to its predecessor **2**. On the other hand, phosphine components, present in composition of compound **2**, does not participate in the formation of product **5**. As a result, compound **5** may be described as a mono-component analogue of **2**, where electroneutrality is reached by the involvement of two additional Na⁺ centers (Figure 6).



Symptomatically the elimination of a phosphine component when using DMSO as reaction medium has been found reproducible. Synthesis in conditions close to the formation of **5** with partial replacement of sodium ions by cesium ones (Scheme 2) resulted in the isolation of trimetallic $Cu_9Na_3Cs_3$ product **6**, also containing no dppe in composition (Figure 7). To our delight, product **6** differs from complex **5** by its ability to pack into 2D coordination polymer net. We suggest that this could be due to the other type of location of cesium ions in the structure of **6** (at "crown ether" positions, coordinated by the hexamembered siloxane rings) in comparison to sodium ions of **5**. As a result, coordination polymer **6**, in comparison to

compounds 1-5, is much less soluble (complexes 1-5 are easily soluble in many polar organic solvents, except for short-chain alcohols).



Solid state structures and Topological analysis

Note, that as for globular and prismatic copper CLMSs^[11b, 12-13] bulky phenyl coating prevents condensation of neighboring cages. None of compounds 1-6 realizes bonding between alkaline atoms of CLMS cage and oxygen atoms of silsesquioxanes of neighboring molecules. At the same time, as some of us previously observed, replacement of sodium atoms with cesium ones favors appearance of coordination polymers,^[13] here, through bridging solvent molecules. In 6, 2D polymers can be found with CLMSs connected through DMSO bridge molecules and fully occupied positions of cesium atoms. The chains are also partially connected through partially occupied positions of cesium atoms to a quiasi-sql net (where CLMSs form a net with topology of a square planar net).

In sense of copper nuclearity, all products reported in this article could be subdivided into three categories: tetra- (complex 1). hexa- (complex 3), and nonanuclear ones (complexes 2-6). The description of topology of the first two types was given by some of us in recent work.^[22] In turn, nonanuclear copper clusters in terms of NDk-m notation^[23] are the 1,2,4M9-1 clusters where 1,2,4 is coordination number of topologically non-equivalent nodes, M denotes a discrete cluster, 9 is the number of metal atoms in the cluster, and 1 is a classification number to distinguish topologically distinct clusters with equal NDk parameters (Fig. 8). In these clusters copper atoms realize three different types of connectivity with different orientation of equatorial and axial planes for connected atoms. Note that this type of clusters was not only absent in CLMSs previously synthesized, but was not met previously in other metal clusters (see TTD collection at http://topospro.com/databases/ttd/).



Figure 8. The nona-Cu-containing clusters connected by bridge atoms in CLMSs 2-6 (a), and the graphs of clusters connectivity (b).

Oxidation of alkanes and alcohols with

Polynuclear copper derivatives are known to constitute active reaction centers of certain (oxidases, particulate methane monooxygenase, (pMMO), α-hydroxylating monooxygenase



Figure Top. Molecular structure of [(PhSiO_{1.5})₁₂(PhSiO_{1.5})₈(CuO)₈(NaO_{0.5})₃(CsO_{0.5}){Cu(O_{0.5})₄}Cs₂] 6 (solvating molecules of DMSO are omitted in the sake of clarity). Center. ChemDraw structure of 6. Bottom, 2D coordination polymer structure of 6.

etc.) oxidizing enzymes.^[24] Various copper complexes play the role of enzyme models^[25], some copper-catalyzed oxidations of cyclohexane were also reported.^[25i] Recently, we have found that coppersilsesquioxanes catalyze efficient oxidations of benzene, alkanes, and alcohols with peroxides.^[20, 22, 26]

In the present study, we report on the interaction of complexes **1** and **4** with peroxides in the presence of alkanes, RH, which afforded oxygenated products, namely alkyl hydroperoxides, ROOH. Secondary alcohols have been catalytically oxidized into ketones.

Kinetic curves for the product accumulation in the cyclohexane oxidation are presented in Fig.9. Dependences of the initial oxidation rate W_0 on initial concentration of the catalyst **4** and cyclohexane are shown in Fig. 10. Heating a solution of cyclohexanol and TBHP in acetonitrile gave cyclohexanone in 72% yield after 5 h (Fig. 11). The oxidation of 1-phenylethanol afforded acetophenone in 76% yield after 10 h (Fig. 12).



Concentration (M)



Figure 9. Top. General scheme for oxidation of cyclohexane. Bottom. The accumulation of cyclohexanol (curve 1) and cyclohexanone (curve 2) in the course of cyclohexane oxidation with H_2O_2 in acetonitrile in air. Conditions. Catalyst **4**, 5×10^{-4} M; cyclohexane , 0.46 M; H_2O_2 (50% aqueous, 2 M). A: at 20 °C; in the presence of HNO₃, 0.05 M; maximum yield of oxygenates is 20% after 1 h; TON = 182. B: at 60 °C; in the presence of HNO₃, 0.1 M. C: at 60 °C; in the absence of HNO₃. In all cases concentrations of the oxygenates were measured after addition of PPh₃ to the reaction sample. ^[27].



Figure 10. The oxidation of cyclohexane with H₂O₂ in acetonitrile in air. Conditions. Catalyst **4**, 5 × 10⁻⁴ M; H₂O₂ (50% aqueous, 2 M) at 60 °C in the presence of HNO₃, 0.05 M. Concentrations of the oxygenates were measured after addition of PPh₃ to the reaction sample.



Figure 11. The accumulation of cyclohexanone (curve 1) in the course of cyclohexanol (0.38 M) oxidation with TBHP (70% aqueous, 1.2 M) by catalyst **4** (5 x 10-4 M) in acetonitrile in air at 60 °C. Maximum yield of oxygenates is 72% after 5 h; TON = 550. Curve 2: the same reaction in the presence of HNO₃, 0.05 M. Concentrations of the ketone were measured after addition of PPh₃ to the reaction sample.



Figure 12. Top. General scheme for oxidation of 1-phenylethanol. Bottom. The accumulation of acetophenone (curve 2) and 1-phenylethanol consumption (curve 1) in the course of 1-phenylethanol (0.5 M) oxidation with TBHP (70% aqueous, 1.2 M) catalysed by 4 ($5 \times 10-4$ M) in acetonitrile in air at 60 °C in the presence of HNO₃, 0.05 M.

We tested also compound **1** in catalytic oxidations of cyclohexane and alcohols. Heating a solution of cyclohexane (0.46 M) and H_2O_2 (2 M) in acetonitrile in the presence of compound **1** (5 × 10⁻⁴ M) at 60 °C during 1 h gave cyclohexanol (0.039 M) and cyclohexanone (0.015 M), total TON = 108. It is noteworthy that in this case addition of HNO₃ (0.05 M) led to a sharp decrease of product yield (0.004 and 0.00027 M of



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cyclohexanol and cyclohexanone, respectively). The reaction of cycohexanol (0.38 M) with TBHP (1.2 M) catalyzed by **1** (5×10^{-4} M) at 60 °C gave after 3 h cyclohexanone (70%). Acetophenone in 94% yield was obtained under the same conditions from 1-phenylethanol (0.49 M).

Catalytic oxidation of alcohols and amines to produce amides

We previously reported the ability of CLMSs to catalyze the oxidative formation of amides from alcohols.^[6c, 22, 28] In the literature, this reaction could be performed using Cu,^[29] Fe^[30] or Zn^[31], but catalyst loading could not be decreased below 1 mol% With the use of CLMSs, this reaction was found efficient with dramatically lower loadings (down to 100 ppm of Cu^[22] and 500 ppm of Fe^[6c, 28]). Since compounds 1 and 4 present really atypical structures, their catalytic activity was also evaluated in the transformation of benzylic alcohol into benzamide. Reactions were performed using as low as 100 ppm of copper and calcium carbonate 99.995% pure to ensure that copper was the only metal responsible for the catalysis. Thus, benzylic alcohol was put in the presence of various primary and secondary amines, tert-butylhydroperoxide as oxidant in refluxing acetonitrile for 24h (Table 1). Of note, the concomitant use of the ammonium salt and calcium carbonate was compulsory to slowly release free amine in the reaction mixture and observe good conversions. Gratifyingly, even though a really low amount of copper was used, desired amides could be isolated in good yields (64 - 84 %). Primary amines (Table 1, entries 1 - 6) were slightly more easily converted than secondary ones (Table 1, entries 7 - 12). CLMSs 1 and 4 behaved similarly under the reaction conditions and excellent TON (turnover number) and TOF (turnover frequency) values, up to 8400 and 350 h⁻¹, respectively, could be obtained. To compare, when 2 mol% of CuO were used in the original report on copper-catalyzed oxidative amidation,^[29a] TON and TOF values did not exceed 44 and 11 h⁻¹, respectively. Hence, low loading CLMS catalysis revealed extremely efficient.

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Table 1. Oxidative amidation at low catalyst loading ^a						
OH +		1 or 4 (100 ppm of Cu) TBHP CaCO ₃		Ph N R^1 R^2		
Ph ²	R ¹	CH ₃ CN, 80°C, 24h				
Entry	Amide	Cat.	Yield (%)	TON/TOF (h ⁻¹) ^{b,c}		
1	о " <i>n-</i> Ви	1	76	7600 / 317		
2	Pn N H	4	77	7700 / 321		
3	°	1	74	7400 / 308		
4	Ph N H	4	68	6800 / 283		
5	0 	1	82	8200 / 342		
6	Ph N Ph H	4	83	8300 / 346		
7		1	67	6700 / 279		
8	Ph N	4	66	6600 / 275		
9		1	64	6400 / 267		
10	Ph ⁺ N O	4	68	6800 / 283		
11		1	77	7700 / 321		
12	Ph ⁺ N ⁺ Ph Ph	4	84	8400 / 350		

[a] Reaction conditions: amine-HCl (0.5 mmol), benzyl alcohol (1.0 mmol), CaCO₃ (99.995% pure; 0.5mmol), TBHP (5.5m in nonane, 2.5 mmol), 1 or 4 (100 ppm of Cu), CH₃CN (1mL), 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} .

Conclusions

Herein, we present a detailed study of novel simple method for cage-like metallasilsesquioxane synthesis. This method implies the use of bidentate phosphine (dppe) ligand as a key reagent in formation of Cu,Na-based cage products of different nuclearity (Cu₄Na₂ and Cu₉Na₄). Involvement of two types of ligands (silsesquioxane and phosphine) is found to be responsible for an unprecedented redistribution of copper ions between two types of ionic components (cage Cu,Na-silsesquioxane and Cu(dppe)₂), forming the whole complex product. This reaction was found to be solvent system sensitive, allowing to isolate additional examples of fascinating (Cu₉Na₆ and Cu₉Na₃Cs₃) cage silsesquioxane architectures. The first example of evaluating of complexes of this family as precatalysts in homogeneous catalysis revealed high activity of the complexes in oxidations with hydrogen peroxide and TBHP. In turn, the catalytic formation of benzamides was found to be promising since as low as 100 ppm of copper, with the use of compounds 1 and 4, allowed to reach TON and TOF up to 8400 and 350 h^{-1} . A further focus on this CLMS synthesis will no doubt open opportunity of discovery of currently unknown structural types of these cage compounds as well as the new possibilities of their catalytic applications.

Experimental Section

Chemicals. $PhSi(OEt)_3$ (98%) and dppe (99%) were purchased from Sigma-Aldrich. Solvents were purchased from Acros.

Synthesis

Compound 1. 1 g (4.16 mmol) of PhSi(OEt)₃ and 0.194 g (4.85 mmol) of NaOH were heated at reflux in 60 ml of ethanol for 1.5 h. Then 0.28 g (2.08mmol) of CuCl₂ was added and resulted blue-colored mixture was stirred without heating for 1 h. Afterward 0.414 g (1.04 mmol) of dppe was added at once and resulted mixture was heated at reflux for 3 h. Hot solution was filtered from precipitate. Crystallization of filtrate gave in 1 week a crystalline material, several single crystals of which were used for X-ray diffraction analysis (1.4EtOH, see below for details). Analysis of complex 1 – calcd. for {(PhSiO_{1.5})₁₂(CuO)₄(NaO_{0.5})₂]Cu(dppe)₄]₂ Si, 9.23; Cu, 10.44; Na, 1.26; P, 6.79. Found (for vacuum dried sample): Si, 9.17; Cu, 10.38; Na, 1.20; P, 6.72. Yield 0.40 g (42 %).

Compound **2**. 1 g (4.16 mmol) of PhSi(OEt)₃ and 0.216 g (5.40mmol) of NaOH were heated at reflux in 60 ml of ethanol for 1.5 h. Then 0.28 g (2.08 mmol) of CuCl₂ was added and resulted blue-colored mixture was stirred without heating for 1 h. Afterwards 0.414 g (1.04 mmol) of dppe was added at once and resulted mixture was heated at reflux for 3 h. Hot solution was filtered from precipitate. Crystallization of filtrate gave in 1 week a crystalline material, several single crystals were used for X-ray diffraction analysis (2·8EtOH·2H₂O), see below for details). Analysis of complex **2** – calcd. for {(PhSiO_{1.5})₁₂(PhSiO_{1.5})₈(CuO)₈(NaO_{0.5})₄[Cu(O_{0.5})₄]}Cu(dppe)₂]₂ Si, 10.89; Cu, 13.55; Na, 1.78; P, 4.80. Found (for vacuum dried sample): Si, 10.81; Cu, 13.46; Na, 1.60; P, 4.71. Yield 0.18 g (17 %).

Compound 3. 1 g (4.16 mmol) of PhSi(OEt)₃ and 0.188 g (4.70 mmol) of NaOH were heated at reflux in 60 ml of ethanol for 1.5 h. Then 0.28 g (2.08 mmol) of CuCl₂ was added and resulted blue-colored mixture was stirred without heating for 1 h. Afterwards 0.414 g (1.04 mmol) of dppe was added at once and resulted mixture was heated at reflux for 3 h. Hot solution was filtered from precipitate. Crystallization of filtrate gave in 1 week a crystalline material, several single crystals were used for X-ray diffraction analysis (3-12EtOH.2H2O), see below for details). Analysis of complex 3 calcd. for {(PhSiO_{1.5})₁₂(PhSiO_{1.5})₈(CuO)₈(NaO_{0.5})₄{Cu(O_{0.5})₄}]Cu(dppe)₂]₂[(PhSiO_{1.5}))12(CuO)6] Si, 12.50; Cu, 15.03; Na, 1.28; P, 3.45. Found (for vacuum dried sample): Si, 12.41; Cu, 14.92; Na, 1.22; P, 3.39. Yield 0.12 g (13 %).

Compound **4**. 1 g (4.16 mmol) of PhSi(OEt)₃ and 0.216 g (5.40 mmol) of NaOH were heated at reflux in 60 ml of ethanol for 1.5 h. Then 0.28 g (2.08 mmol) of CuCl₂ was added and resulted blue-colored mixture was stirred without heating for 1 h. Afterwards 0.414 g (1.04 mmol) of dppe dissolved in 45 ml of toluene was added at once and resulted mixture was stirred for 2 h. Solution was filtered from precipitate. Crystallization of filtrate gave in 2 weeks a crystalline material, several single crystals were used for X-ray diffraction analysis (4•6EtOH.2H₂O.2C₇H₈), see below for details). Analysis of complex **4** - calcd. for [(PhSiO_{1.5})₁₂(PhSiO_{1.5})₈(CuO)₈(NaO_{0.5})₄(Cu(O_{0.5})₄)][Cu(dppe)₂]₂ Si, 10.89; Cu, 13.55; Na, 1.78; P, 4.80. Found (for vacuum dried sample): Si, 10.81; Cu, 13.46; Na, 1.60; P, 4.71. Yield 0.49 g (46 %).

Compound **5**. 1 g (4.16 mmol) of PhSi(OEt)₃ and 0.216 g (5.40 mmol) of NaOH were heated at reflux in 50 ml of ethanol for 1.5 h. Then 0.28 g (2.08 mmol) of CuCl₂ was added and resulted blue-colored mixture was stirred without heating for 1 h. Afterwards 0.414 g (1.04 mmol) of dppe and 60 ml of dmso were added at once. Resulted mixture was brought at reflux along with simultaneous distillation of the solution to completely remove ethanol from the reaction mixture. When ~45 mL of distillate was collected, the mixture was cooled to room temperature and filtered from precipitate. Crystallization of filtrate gave in 2 weeks a crystalline material,

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several single crystals were used for X-ray diffraction analysis (5•8DMSO), see below for details). Analysis of complex **5** – calcd. for [(PhSiO_{1.5})₁₂(PhSiO_{1.5})₈(CuO)₈(NaO_{0.5})₄{Cu(O_{0.5})₄}Na₂] Si, 16.12; Cu, 16.41; Na, 3.96; P, 0.0. Found (for vacuum dried sample): Si, 16.06; Cu, 16.32; Na, 3.870; P, 0.0. Yield 0.14 g (19 %).

Compound 6. 1 g (4.16 mmol) of PhSi(OEt)₃ and 0.216 g (5.40 mmol) of NaOH were heated at reflux in 50 ml of ethanol for 1.5 h. Then 0.28 g (2.08 mmol) of CuCl₂ was added and resulted blue-colored mixture was stirred without heating for 1 h. Afterwards 0.414 g (1.04 mmol) of dppe and 60 ml of dmso were added at once. Resulted mixture was brought at reflux along with simultaneous distillation of the solution to completely remove ethanol from the reaction mixture. When ~45 mL of distillate was collected, 0.43 g (2.83 mmol)of CsF was added at once to mixture. Resulted solution was heated at reflux for additional 3 h, then cooled to room temperature and filtered from precipitate. Crystallization of filtrate gave in 2 weeks a crystalline material, several single crystals were used for X-ray diffraction analysis (5•9DMSO), see below for details). Analysis complex 6 calcd. of for [(PhSiO_{1.5})₁₂(PhSiO_{1.5})₈(CuO)₈(NaO_{0.5})₃(CsO_{0.5}){Cu(O_{0.5})₄}Cs₂] Si, 14.72; Cu, 14.99; Na, 1.81;Cs, 10.45; P, 0.0. Found (for vacuum dried sample): Si, 14.65; Cu, 14.90; Na, 1.71; Cs, 10.37; P, 0.0. Yield 0.12 g (15 %).

IR studies of the bulky samples of crystalline materials of **1-6** were carried out on a Shimadzu IRPrestige-21 FTIR spectrometer (KBr) in the 600–4000 cm⁻¹ range. IR spectra are given in ESI.

Oxidation of Alcohols and Alkanes

The reactions of alcohols were carried out in air in thermostated Pyrex cylindrical vessels with vigorous stirring and using MeCN as solvent. The substrate was then added and the reaction started when the oxidant was introduced in one portion. Concentrations of products obtained in the oxidation of 1-phylethanol after certain time intervals were measured using ¹H NMR method (solutions in acetone- d_6 ; "Bruker AMX-400" instrument, 400 MHz). In the oxidation of cyclohexanol, concentrations of the substrate and products were measure by chromatography as described below for the oxidation of cyclohexane.

Oxidations of alkanes was carried out analogously. Catalysts 1 or 4 as well as the co-catalyst (nitric acid) were introduced into the reaction mixture in the form of stock solutions in acetonitrile. The alkane was then added and the reaction started when hydrogen peroxide was introduced in one portion. (CAUTION. The combination of air or molecular oxygen and H_2O_2 with organic compounds at elevated temperatures may be explosive!). The reaction solutions after addition of nitromethane as a standard compound were analyzed by GC. Instrument LKhM-80-6 was used (columns 2 m with 5% Carbowax 1500 on 0.25-0.315 mm Inerton AW-HMDS; carrier gas argon) for measuring concentrations of cyclohexanol and cyclohexanone. The samples of reaction solutions were in some cases analyzed twice: before and also after their treatment with PPh₃. This method (an excess of solid triphenylphosphine is added to the samples 10-15 min before the GC analysis) proposed previously by one of us^[27] allows us to detect alkyl hydroperoxides and to measure also the real concentrations of all three products (alkyl hydroperoxide, alcohol and aldehyde or ketone) really present in the reaction solution, because usually alkyl hydroperoxides are decomposed in the gas chromatograph to produce mainly the corresponding alcohol and ketone. It is necessary to emphasize that the phosphine is added mainly to compare intensities of cyclohexanol and cyclohexanone peaks but not only to reduce remaining H2O2. The comparison gives us the real concentration of cyclohexyl hydroperoxide in the reaction mixture. In our kinetic studies described below, in order to determine the initial reaction rate W_0 we measured concentrations of cyclohexanone and cyclohexanol only after reduction of the reaction mixture with PPh3 which gives precisely concentration of a sum of the oxygenates. Blank experiments with cyclohexane showed that in the absence of catalysts $\mathbf{1}$ and $\mathbf{4}$ no products were formed.

Amides synthesis

General considerations

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 300 MHz spectrometer. Chemical shifts are reported in ppm and referenced to the solvent peak (CDCl₃ at 7.26 ppm). Data are reported as 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 Bruker Avance AM 126 MHz spectrometer. Chemical shifts are reported to the solvent peak (CDCl₃ at 77.16 ppm).

General procedure

In a sealed tube were added successively amine hydrochloride (0,5mmol), CaCO₃ (50.1 mg, 0.5 mmol), CH₃CN (1mL), **1** (20 μ L of a solution of 3,0mg of **1** in 2mL of CH₃CN) or **3** (20 μ L of a solution of 1.8 mg of **3** in 2mL of CH₃CN), benzylic alcohol (105 μ L, 1.0 mmol) and TBHP (5.5M in nonane, 225 μ L, 1.25mmol). The mixture was stirred at 80°C for 2h and TBHP (5.5M in nonane, 225 μ L, 1.25mmol) were again added to the mixture. After 22h at 80°C, the mixture was cooled to room temperature and 1N HCl and AcOEt were added. The mixture was extracted twice with AcOEt, 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 were added and evaporated under reduced pressure. Crude product was then purified using silica gel chromatography using gradients of cyclohexane/AcOEt to yield the pure compounds.

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Keywords: cage complexes • metallasilsesquioxanes • amidation • C-H compounds' oxidation• X-ray

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Ionic Complexes of Tetra- and Nonanuclear Cage Cu(II)phenylsilsesquioxanes: Synthesis and High Activity in Oxidative Catalysis

Novel approach to cage metallasilsesquioxanes using self-assembling reactions with participation of dppe as a key reactant is suggested. An unique family of complexes which include anionic cage Cu(II),Na-silsesquioxane and cationic Cu(I)dppe₂ components is achieved this way. An application of synthesized complexes as catalysts revealed their very high activity in homogeneous oxidation of alkanes and alcohols to produce alkyl hydroperoxides, ketones and amides.

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