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Research Article

Hexacoppergermsesquioxanes as complexes with N-ligands: synthesis, structure and catalytic properties

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We dedicate this paper to our dear friend and colleague Prof. Armando José Latourrette de Oliveira Pombeiro.

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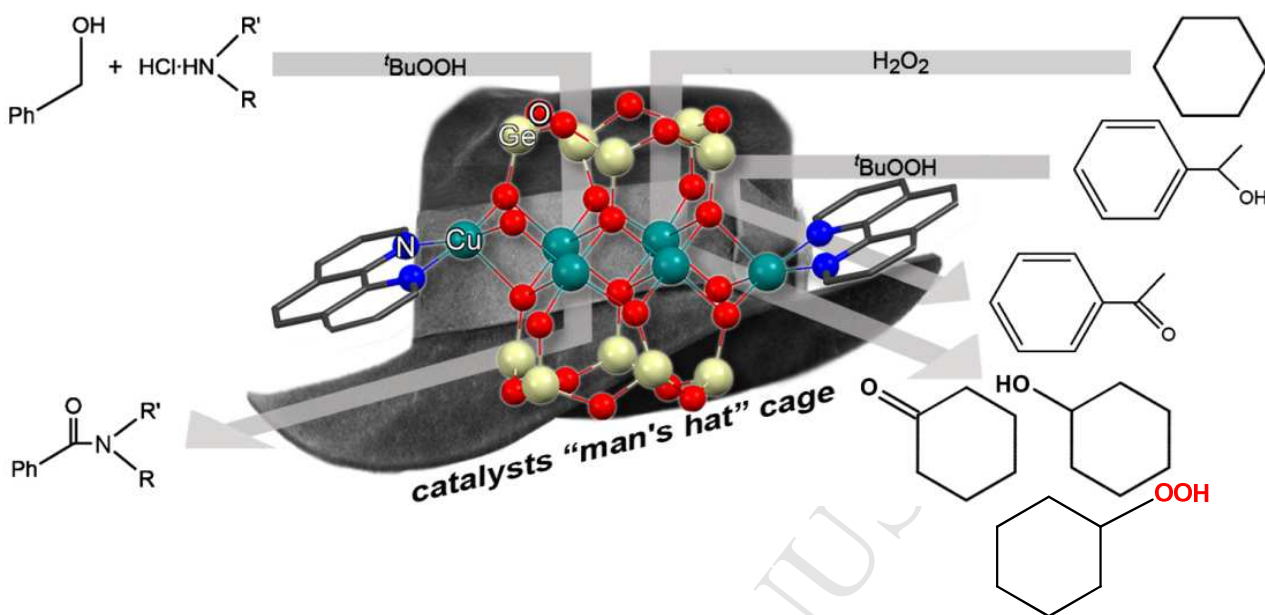
Highlights

- New hexanuclear coppersilsesquioxanes have been synthesized
- The structures of complexes in crystals have been determined
- The complexes are good catalysts in oxidation of alkanes and alcohols with H₂O₂ or *tert*-butyl hydroperoxide
- Hydroxyl radicals take part in the reaction

ABSTRACT

A simple and versatile strategy of synthesis of cage metallagermaniumsilsesquioxanes is demonstrated for isolation of Cu₆-based phenylgermsesquioxanes **1-6**. Structure of newly synthesized coppergermsesquioxanes was established by single-crystal X-ray diffraction analysis. General principle of these cages' topology implies the presence of two linear Cu₃ fragments, coordinated by three pairs of ligands. These are: (i) cyclic germesquioxanes [PhGeO_{1.5}]₅, products **1-6**, (ii) 1,10-phenanthrolines, (**1**, **3-5**) or 2,2'-bipyridines, (**2**, **6**), (or and (iii) OX species (X = H, **1-2**, CH₃, **3**, H and C₂H₅O, **4**, HCO, **5**, CH₃CO, **6**). Appearance of non-expected species (formate for **5**, acetate for **6**), resulted from corresponding alcohols used as reaction media, points at easyness of oxidation processes in the conditions of such self-assembling reactions. Catalytic tests showed high activity of complexes **1** and **2** as precatalysts in homogeneous oxidations of alkanes (cyclohexane, methylcyclohexane, *n*-heptane, *cis*-1,2-dimethylcyclohexane with hydrogen peroxide in acetonitrile solution. Hydroxyl radicals take part in the reaction. The same complexes catalyze oxidation of alcohols (cyclohexanol, 2-heptanol, 1-phenylethanol) to corresponding ketones with *tert*-butyl hydroperoxide in almost 100% yield. With the addition of various alkyl ammonium salts, complex **2** could also furnish corresponding amides in high yield.

Graphical Abstract:



1. Introduction

Multinuclear complexes are among the most efficient catalysts for chemical processes of high demand [1-6]. Multinuclearity's main advantages are well known: (i) opportunity of the realization of multi-electron processes [7-9]; (ii) selectivity [10-12]; (iii) higher activity than for mononuclear catalysts [13-16]; (iv) cooperative interactions [17-19], especially prominent in case of involvement of metal ions with different Lewis acidity [20-22]. Significant benefits in the field are brought by the use of cage-like compounds, combining metal centres and functional ligands in the frameworks of multiple topologies. Regarding the latter, it is worth to emphasize the specific organisation of cage' components, giving synergistic effects for impressive catalytic applications [23-31]. Among other types of metallocages, significant attention has been paid to those constructed from branched organoelement, sesquioxane, blocks (RXO_{1.5}). Metallasilsesquioxane (X = Si) compounds, firstly discovered in 1986 [32-33], are thoroughly described in several book chapters and reviews [34-44], including numerous examples of their catalytic activity [41, 45-49]. In turn, metallasilsesquioxanes' close analogues, metallagermsesquioxanes (X = Ge), still remain in the shadow. Hydrothermal method was reported for isolation of MOF-like objects starting from germanium sesquioxide [50-59]. Some of these products were isolated in the presence of additional ligands, namely 2-picolinic acid [50, 56-57], 2-pyrazinecarboxylic acid [56-57], 2,6-pyridinedicarboxylic acid [57] or 1,10-

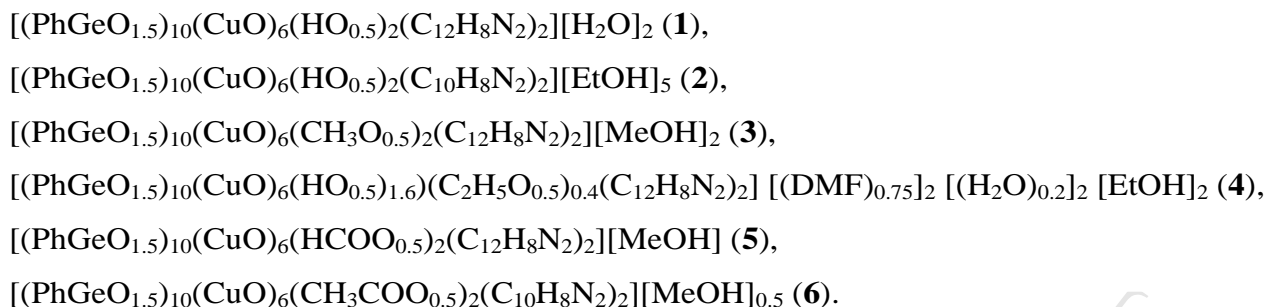
phenanthroline [58-59]. These unusual products demonstrated luminescent [50, 51, 56-57, 59] sorption (of Ar gas [50]) properties and high thermal stability [50-59].

In turn, an alternative approach to individual cage-like metallagermsesquioxanes was developed by some of us recently [60-62]. This method is based on use of reactive germane PhGe(OMe)_3 species and represents several important features such as mild conditions of synthesis and opportunity of isolation of bimetallic (Fe/Na [60], Fe/Cu [61], Ni/Na [62]) products. First representatives of this new class of metallagermsesquioxanes exhibit unusual (spin glass) magnetic behaviour [62] and possess high catalytic activity [63].

Taking in mind positive results, presented recently by some of us for catalytic properties of Cu-phenylsilsesquioxanes bearing additional N-ligands, namely 2,2'-bipyridine and 1,10-phenanthroline [64], we were interested in synthesis of Cu-based compounds including at the same time two types of metal' surrounding, (i) phenylgermsesquioxane and (ii) ligand of 2,2'-bipy family. Known prominent metallic character of germanium, according to our expectations, could provide higher activity of such compounds in comparison to silicon-based predecessors. For the catalysed reactions we chose two processes of highest interest, namely: (i) amidation and (ii) oxidation of C-H compounds. The first reaction is known as a key reaction for contemporary green chemistry, requiring solutions for minimization of waste production [65]. Several high efficient catalytic systems (on base of Ru [66-68] or Rh [69]) were suggested for the amides formation from alcohols and amines [66-67] or via reductive amidation of aldehydes without an external hydrogen source [68-69]. Recently, an alternative approach, an oxidative amidation of alcohols, was developed. This method implies an use of cheap metal-based complexes (Cu [70-72], Fe [73-76], Zn [77]). The catalyst loading in these reactions, though, could not be decreased below 1%. In turn, as some of us showed previously [78], an application of copper silsesquioxanes allow to work effectively even at 100 ppm of Cu loading.

Regarding the second process of interest, C-H compounds functionalization, the role of metallacomplexes for its catalysis could not be overestimated [79-82]. Along with numerous examples of expansive metal-based (e.g. Au [83], Ir [84], Os [85-86], Pd [87-88], Rh [89-90]) catalysts used for such transformations, several successful efforts were reported for an application of the less expansive metals' complexes, e.g. Co [91], Cu [92], Fe [93], Ni [94]. Important to emphasize that significant amount of publications witness higher catalytic activity of multinuclear complexes in comparison with mononuclear ones [6, 95-96].

In the present study, we have developed the self-assembly approach to Cu(II)-cage complexes, bearing two types of ligands, namely, O-based anionic phenylgermsesquioxanes $[\text{PhGe(O)O}^-]_5$ and N-based bidentate 2,2'-bipyridines (or 1,10-phenanthrolines):

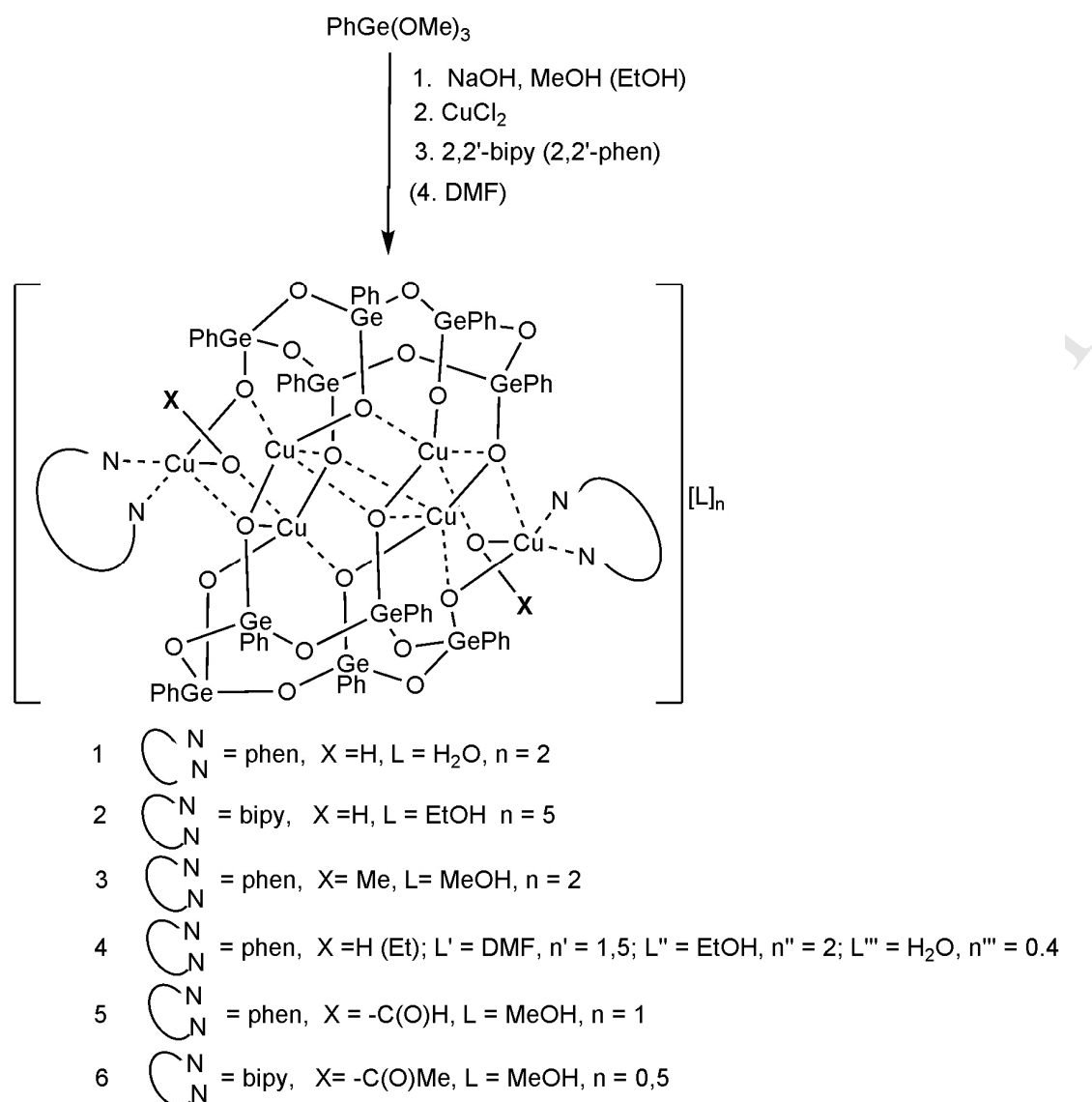


An application of the isolated Cu_6 -phenylgermsesquioxanes **1** and **2** in homogeneous catalysis of oxidative amidation and C-H functionalization turned to be very prospective both in terms of catalyst' activity and minimization of loading.

2. Results and discussion

Synthesis and structure of Cu_6 -phenylgermsesquioxanes containing N-ligands

For the method of synthesis of target mixed-ligand Cu-complexes, we chose an interaction of CuCl_2 at room temperature with a product of alkaline hydrolysis of $\text{PhGe}(\text{OMe})_3$ in methanol/ethanol solution, followed by complexation with corresponding bidentate N-ligand (2,2'-bipyridine or 1,10-phenanthroline). This approach allowed us to get a family of complexes of the same, Cu_6 , nuclearity and composition of Ge-based ligands, $[\text{PhGe}(\text{O})\text{O}^-]_5$ **1-6** (Scheme 1, Fig. 1). The general type of structure remained the same in conditions of crystallization of product from DMF media (complex **4**) instead of typical (alcohol-containing) system used for isolation of **1-3** and **5-6**.



Scheme 1. General scheme of synthesis of hexacoppergermsesquioxanes **1–6** containing additional N-ligands (1,10-phenanthroline or 2,2'-bipyridine)

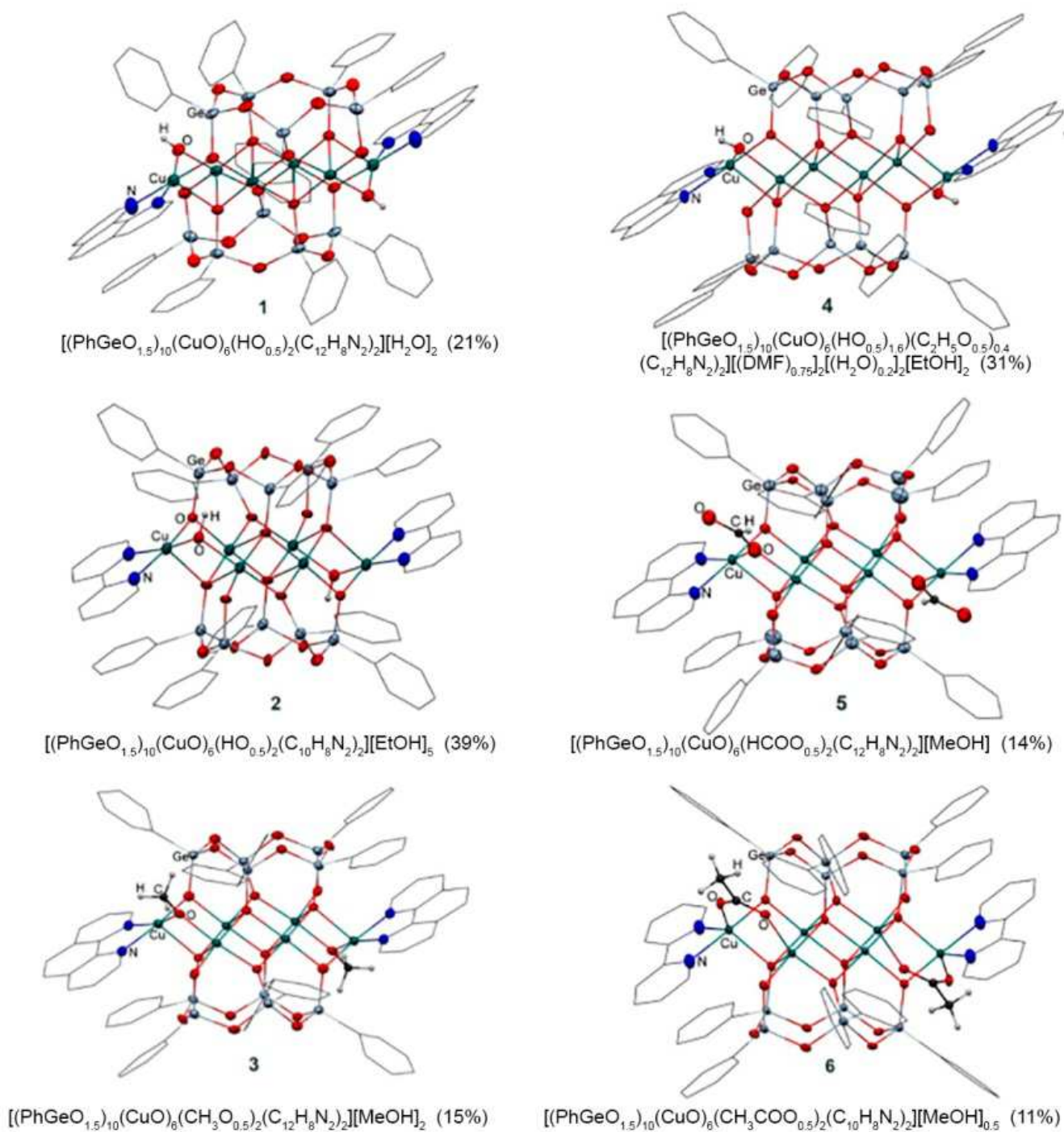


Figure 1. Molecular structure, formula and yields of compounds 1–6.

Regarding the composition of products **1-6**, it is clear that observed feature (six Cu^{2+} cations vs. two Ge-ligands, bearing 10 negative charges) is not adequate from the positions of formal charge balance. Indeed, two additional negative charge carriers are presented in each product structure. These additional anionic groups are as follows: HO^- (compounds **1-2**), CH_3O^- (**3**), HCOO^- (**5**), CH_3COO^- (**6**). In case of compound **4** we observed superposition of several (HO^- and $\text{CH}_3\text{CH}_2\text{O}^-$) groups (1.6/0.4).

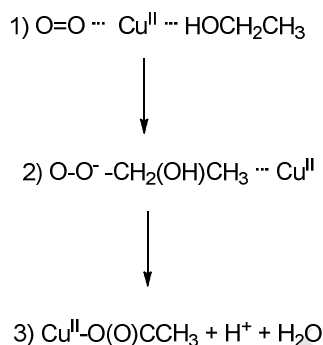
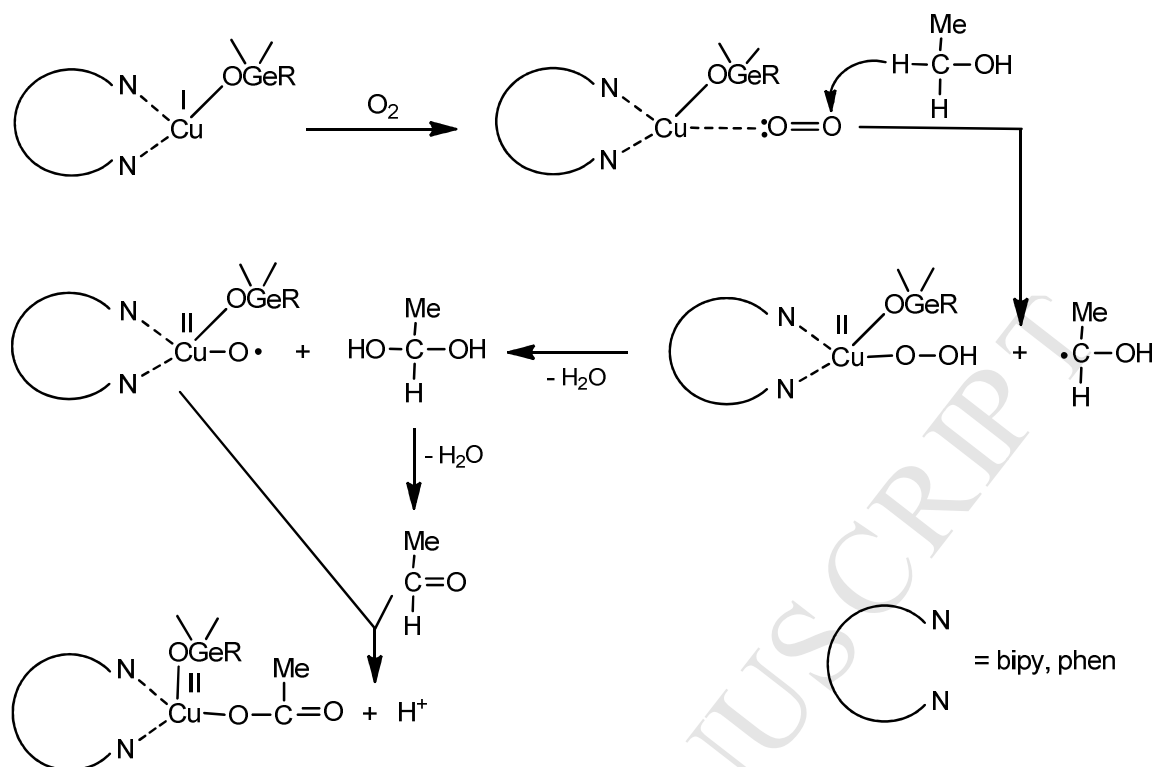


Fig. 2. Presumable scheme of oxidation of alcohols (on the example of ethanol) to the carboxylic acid in the presence of Cu centers of germesquioxane.

The presence of hydroxyl fragments as well as methoxy or ethoxy groups could be easily explained by the water/alcohol presence in the reaction media. In turn, an appearance of carboxylic units is much more unusual. We suggest that formiate (in **5**) and acetate (in **6**) groups were formed as products of oxidation of corresponding, MeOH or EtOH, alcohols (Figure 2). A possible mechanism is presented in Scheme 2. That is quite possible due to the presence of air during synthesis/crystallization of **5-6** (complexes **1-4** were obtained under inert atmosphere).



Scheme 2. A proposed mechanism for the oxidation of ethanol to afford acetate ligand.

This “oxidative” effect has never been observed for metallagermsesquioxanes, while some reports concerning oxidation properties of metallasilsesquioxanes are available. These works reported, e.g. Ce^{III} (to Ce^{IV}) [97], U^{IV} (to U^{VI}) [98], Cr^{II} (to Cr^{IV}) [99] and Cu^{I} (to Cu^{II}) [100] oxidations observed in the course of synthesis of corresponding silsesquioxanes. Intriguing mild-conditioned, “ferment-like”, oxidation of methyl group of neocuproine (into diol fragment) was reported for the self-assembly reaction of Cu-silsesquioxane [101]. In close parallel to presenting work, several examples of solvent’ oxidation were reported as well: tetrahydrofuran to γ -butyrolactone (in the course of Fe-silsesquioxane synthesis) [102], ethanol to acetate (in the course of Cu-silsesquioxane synthesis) [64, 103-104].

In the context of other features of **1-6**’ molecular structure, some points are to be emphasized. First of all, differences in the structure of **1-6** provoked some deviations in copper ions locations (Fig. 3), e.g. the longest Cu...Cu distance varies from 8.01 Å (in **2**) to 8.20 Å (in **6**), while Cu...Cu...Cu angle in Cu-trimers varies from 173.6 deg (in **6**) to 175.7 deg (in **2**).

Secondly, complexes **1-6** include germoxanolate fragments of the same composition $[\text{PhGe}(\text{O})\text{O}]_5$. These fragments consist from two types of oxygen atoms: (i) ones belonging to cyclic -Ge-O-Ge- “germoxane” fragments, (ii) ones belonging to -Ge-O-Cu- “germanolate” fragments (Fig. 4). Difference in geometries of products could be also concluded from the deviation of longest Ge...O

distance in cyclic germoxane fragments (Fig. 3), varying from 5.471 Å (in **2**) to 5.650 Å (in **3**). It was of interest to compare an influence of additional structural factors on the cage geometry.

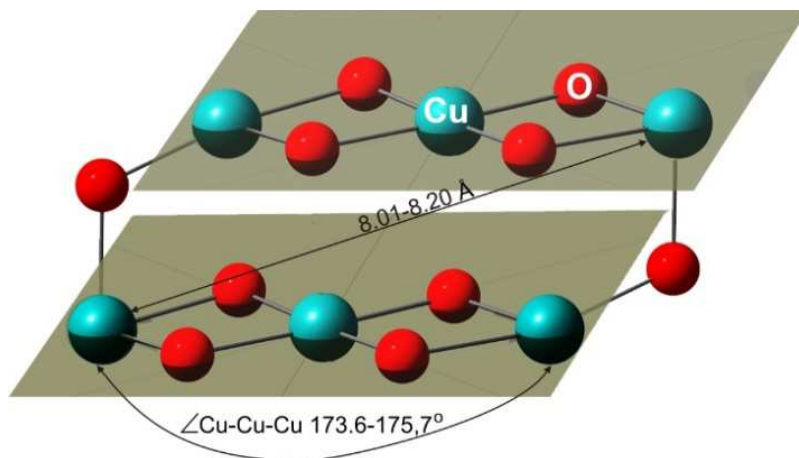


Fig. 3. Location of Cu centers in **1-6**.

This could be done through discussion of the connectivity of two neighbouring copper centers (Figs. 5-7). It was found that distance between peripheral copper ion (coordinated by N-ligand) and near copper ion inside the cage is quite sensitive to nature of oxygen atom bridging them. These oxygen atoms, in turn, are fragments of “charge balancing” groups OX, mentioned above [CuOX, X = H, Me, Et, CR(O), R= H, Me]. Symptomatically that in case of OH fragment (in **4**), possessing highly basic oxygen atom, a maximum shortening of Cu-Cu distance occurred (Fig. 5). Fragment OMe fragment (in **3**) provokes the lengthening of this distance (Fig. 6). Finally, Cu-Cu contact reached its maximum value in case of the OCR(O) fragment’ presence (in **6**) (Fig. 7)

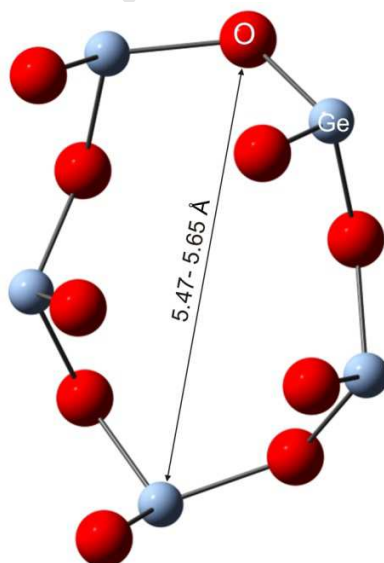


Fig. 4. Structure of Ge-ligands in **1-6**.

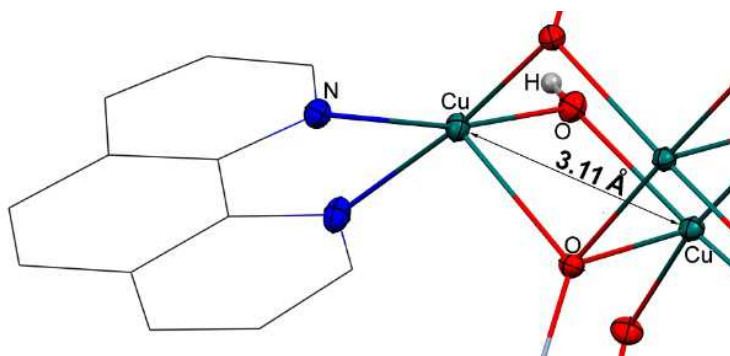


Fig. 5. Structural unit in structure of **4**, describing distortion of molecular architecture.

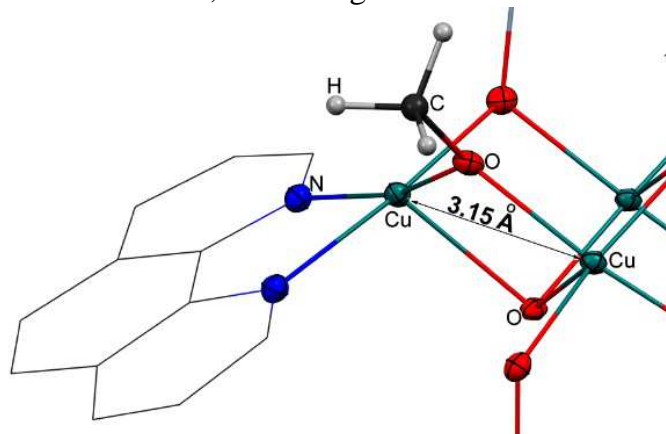


Fig. 6. Structural unit in structure of **3**, describing distortion of molecular architecture.

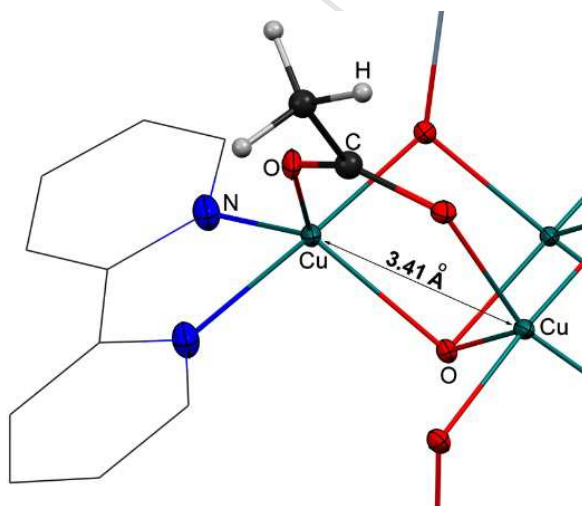


Fig. 7. Structural unit in structure of **6**, describing distortion of molecular architecture.

Crystallographic data for **1–6** have been deposited with the Cambridge Crystallographic Data Center, CCDC 1888654-1888659. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

We used catalysts **1** and **2** for the oxidation of alkanes and alcohols under mild conditions. Hydrogen peroxide and *tert*-butyl hydroperoxide were employed as oxidants acetonitrile was a solvent.

Hydroperoxidation of alkanes with H_2O_2

We have found that cyclohexane can be converted into cyclohexyl hydroperoxide in the presence of catalyst **2** which is gradually transformed in a mixture of cyclohexanol and cyclohexanone in the course of the oxidation (Fig. 8).

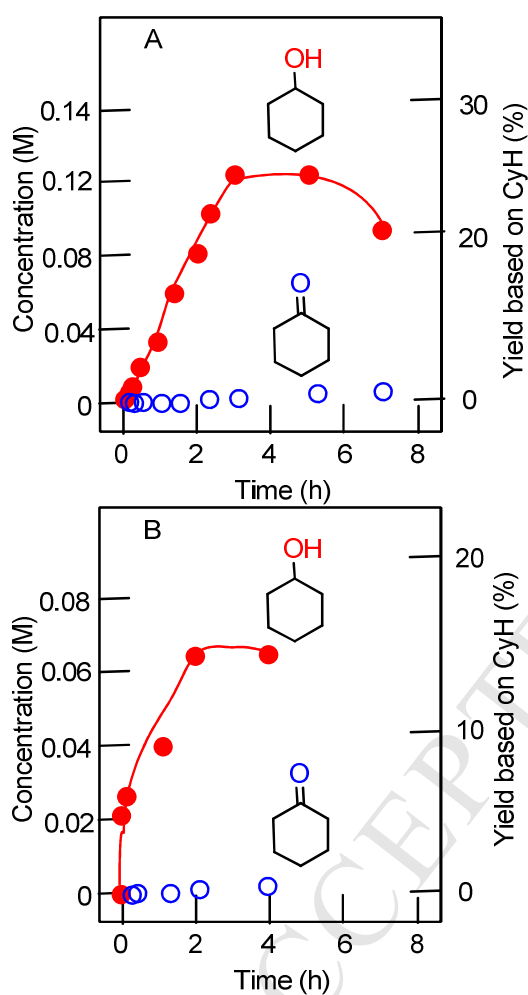


Fig. 8. Accumulation of cyclohexanol and cyclohexanone with time in the oxidation of cyclohexane (initial concentration was 0.46 M) with H_2O_2 (50% aqueous; initial concentration 2 M) catalyzed by compound **2** (5×10^{-4} M), in the presence of HNO_3 (0.05M, Graph A) and in the absence HNO_3 (Graph B). Solvent was acetonitrile (total volume of the reaction solution was 5 mL); 50 °C. All samples were reduced by PPh_3 before GC.

The oxidation of *cis*-1,2-dimethylcyclohexane with H₂O₂ occurs without retention of configuration (the *trans/cis* ratio was 0.8 where the *trans/cis* is the ratio of isomers of *tert*-alcohols with mutual *trans*- and *cis*-orientation of the methyl groups). Regioselectivity parameters in the oxidation of *n*-heptane catalyzed by complex **2** are given in Table 1. Concentrations of products (isomeric alcohols) were measured after reduction with PPh₃. The parameter C(1):C(2):C(3):C(4) is given after normalization which takes into account the number of hydrogen atoms at each carbon. The parameter of bond-selectivity in oxidation of methylcyclohexane 1°:2°:3° = 1.0:5.4:16.0. All these parameters indicate that the oxidation with H₂O₂ occurs with the participation of free hydroxyl radicals [105-107]. It is important to note that catalyzed by **2** oxidation of *cis*-1,2-dimethylcyclohexane with *meta*-CPBA occurs stereoselectively (the *trans/cis* ratio was 0.3; (we found previously analogous effect; see, for example, ref. [108]).

Table 1

Oxidation of *n*-heptane (0.5 M) with H₂O₂ (50% aqueous, 2 M) catalyzed by complex **2** (5×10^{-4} M) in the presence of HNO₃ (0.05 M) at 50 °C.

Entry	Time (min)	C(1):C(2):C(3):C(4) <Total yield of oxygenates, %>
1	60	1.0:6.25:6.25:5.60 <12>
2	120	1.0:3.6:3.6:4.3 <12>
3	180	1.0:6.4:6.4:6.4 <12>

Complex **2** catalyses also the oxidation with H₂O₂ of benzene to phenol (Fig. 9) and with TBHP of cyclohexanol to cyclohexanone (Fig. 10). Oxidation of 1-phenylethanol catalysed by **2** gave acetophenone in 98% yield after 9 h at 50 °C. Dependence of initial oxidation rate on initial concentration of cyclohexane is shown in Fig. 11.

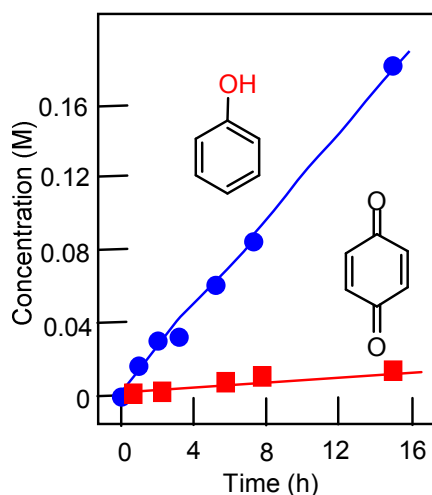


Fig. 9. Oxidation of benzene (0.45 M) to phenol and *p*-quinone with H₂O₂ (2 M; 50% aqueous) catalyzed by **2** (5×10^{-4} M) in the presence of HNO₃ (0.05M) in MeCN at 50 °C. All samples were reduced by PPh₃ before GC.

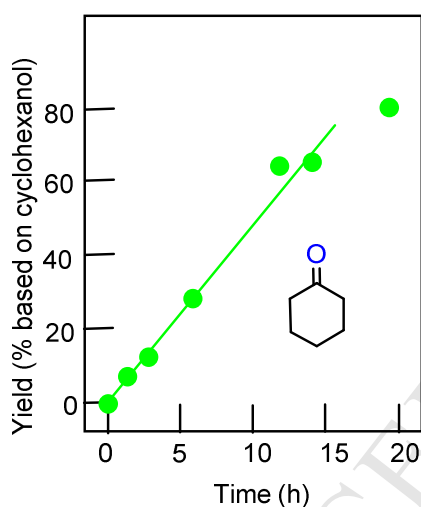


Fig. 10. Oxidation of cyclohexanol (0.23 M) to cyclohexanone with TBHP (1.2 M; 70% aqueous) catalyzed by **2** (5×10^{-4} M) in the presence of HNO₃ (0.05M) in MeCN at 50 °C. All samples were reduced by PPh₃ before GC.

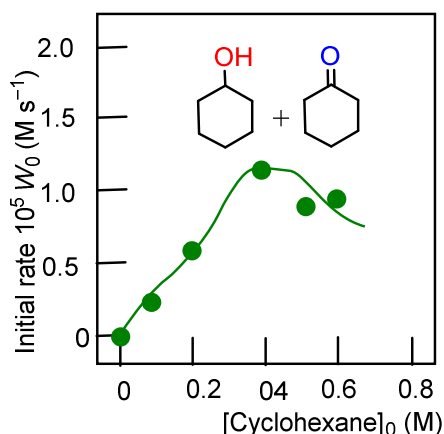


Fig. 11. Dependence of the initial rate W_0 of oxygenate accumulation in the cyclohexane oxidation with H_2O_2 catalyzed by **2** in MeCN on the initial concentration of cyclohexane. Conditions: H_2O_2 (50% aqueous; initial concentration 2 M), compound **2** (5×10^{-4} M), in the presence of HNO_3 (0.05M). Solvent was acetonitrile (total volume of the reaction solution was 5 mL); 50 °C. All samples were reduced by PPh_3 before GC.

Complex **1** turned also out to be an efficient catalyst. The data given in Fig. 12 indicate that the oxidation of cyclohexane with H_2O_2 proceeds with the formation of cyclohexyl hydroperoxide which in the course of the reaction decomposes in part to afford cyclohexanol and cyclohexanone [109-118]. In the presence of catalytic amounts of complex **1**, tert-butyl hydroperoxide oxidizes 1-phenylethanol and 2-heptanol into acetophenone and 2-heptanone, respectively (Fig. 13).

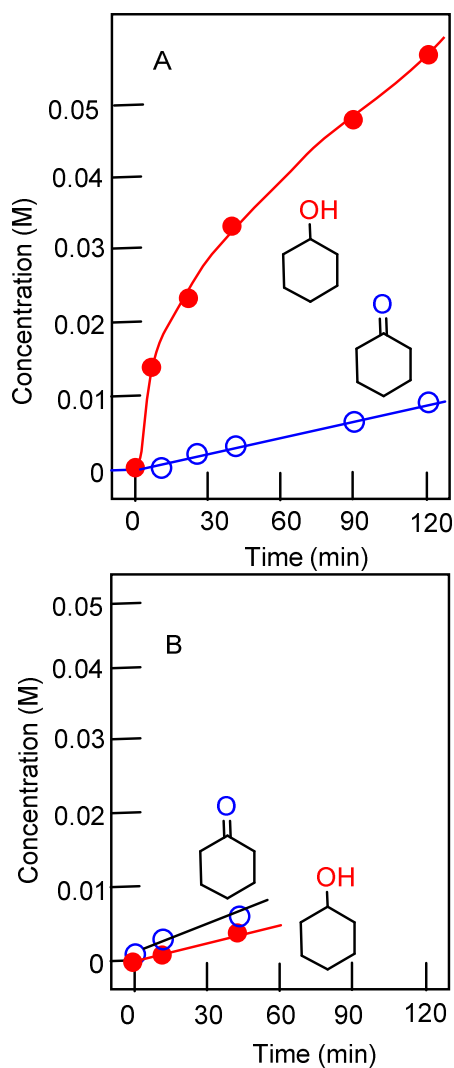


Fig. 12. Accumulation of cyclohexanol and cyclohexanone with time in the oxidation of cyclohexane (initial concentration was 0.23 M) with H_2O_2 (50% aqueous; initial concentration 1.5 M) catalyzed by compound **1** (5×10^{-4} M), samples were either reduced by PPh_3 before GC (Graph A) or were not treated with PPh_3 before GC (Graph B) (for this method see refs. [109-118]). Solvent was acetonitrile (total volume of the reaction solution was 5 mL); 50 °C. Total yield of cyclohexanol and cyclohexanone after 120 min and reduction with PPh_3 was 29%.

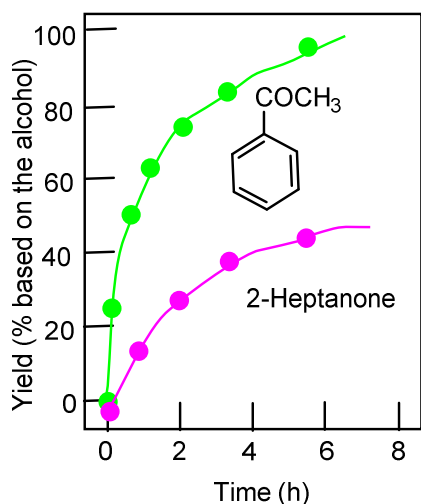
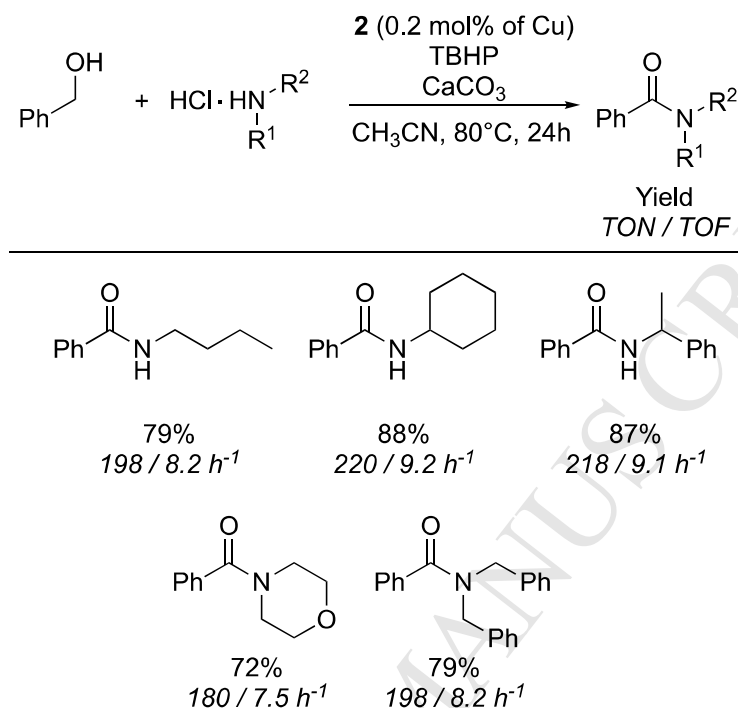


Fig. 13. Oxidation of 1-phenylethanol (0.16 M) and 2-heptanol (0.23 M) to acetophenone and heptanone-2, respectively, with TBHP (1.2 M; 70% aqueous) catalyzed by **1** (5×10^{-4} M) in the presence of CF_3COOH (0.05M) in MeCN at 50 °C. All samples were reduced by PPh_3 before GC.

Having good results in hand for oxidation of alkanes and alcohols using peroxides, complex **2** was evaluated in the formation of amides starting from alcohols and amines. Indeed, this reaction was already described using copper [119], iron[120-123] and zinc[124] salts, but also cage-like copper and iron compounds[60, 61, 64]. As already demonstrated in literature, the formation of amides involves an oxidation of benzylic alcohol into corresponding aldehyde, reaction with the amine to form a hemiaminal, which is further oxidized into amide. Of note, the amines have to be protected as their hydrochloride salt, and deprotonated *in situ*, in order to avoid side reaction with TBHP. In a view for comparison with our previous reports on oxidative amidation using cage compounds, reaction conditions optimized previously were directly adapted to the use of compound **2**. Benzyl alcohol was reacted with the appropriate ammonium chloride salts in the presence of TBHP as oxidant and calcium carbonate as a weak base (Scheme 3). Interestingly, reactions could be performed using as low as 0.2 mol% of copper in the reaction mixture, thanks to the good solubility of **2** in acetonitrile, and still provide high yields of desired amides. Secondary amides, starting from the hydrochloride salts of *n*-butyl, cyclohexyl, and (\pm)- α -methylbenzylamine, were isolated in 79 – 88 % yield. Formation of tertiary amides was slightly less efficient and compounds featuring morpholine and dibenzylamine could be obtained in 72 and 79% yield, respectively. Turnover number (TON) and frequency (TOF) were calculated to evaluate the efficiency of the catalyst in this reaction. Even though TOF values were not as high as in previous reports, TON values were interesting in

comparison with our seminal report on CuO-catalyzed. Indeed, in the presence of CuO, TON values reach a maximum at 44 [119]. Thanks to the use of complex **2**, catalyst loading could be reduced to 0.2 mol% of Cu and TON values up to 220 could be obtained.



Scheme 3. Oxidative amidation of alcohols and amines using **2** as catalyst

3. Experimental Section

Materials and Methods

All the chemicals were of analytical grade and used as received. PhGe(OMe)₃ was purchased from ABCR. XRF analysis was performed using a spectrometer VRA-30. IR spectra were recorded on Shimadzu IR Prestige21 FTIR spectrometer in KBr pellets ($\nu_{\text{Ge-Ph}}$ 1100 cm⁻¹; $\nu_{\text{as Ge-O}}$ 840-820 cm⁻¹; $\nu_{\text{s Ge-O}}$ 950 cm⁻¹; $\sigma_{\text{C-H}}$ of mono-substituted phenyl groups 680-670 cm⁻¹, $\delta_{\text{Ge-O}}$ 459 cm⁻¹).

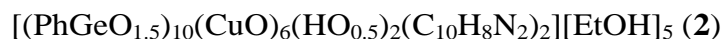
Syntheses of **1-4** were performed under nitrogen atmosphere.

Syntheses of Cu₆-phenylgermsesquioxanes containing N-ligands

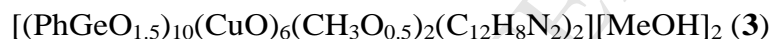
[(PhGeO_{1.5})₁₀(CuO)₆(HO_{0.5})₂(C₁₂H₈N₂)₂][H₂O]₂ (**1**)

PhGe(OMe)₃ (1.20 g; 4.9 mmol) in 60 ml of an ethanol/methanol (1:1) solution was mixed with solid NaOH (0.24 g; 5.9 mmol). Mixture was heated under reflux for 2 h. Afterwards, the solution was cooled to room temperature and 0.40 g (3.0 mmol) of anhydrous CuCl₂ was added at once. The solution was left under stirring overnight and 0.18 g (0.9 mmol) of 1,10-phenanthroline were added. Resulted mixture was left under stirring for 4 h and then

filtered from the insoluble part. The filtrate was stored in a warm place in a flask equipped by septum with two needles to admit a slow current of nitrogen and evaporation of the solvents. After approximately 7 days the formation of crystalline material **1** was occurred; a few selected single crystals were used for the X-ray diffraction analysis (see ESI for details). Anal. Calcd for $[(\text{PhGeO}_{1.5})_{10}(\text{CuO})_6(\text{HO}_{0.5})_2(\text{C}_{12}\text{H}_8\text{N}_2)_2]$ Cu, 14.70; N, 2.16; Ge, 28.01. Found (for vacuum-dried sample): Cu, 14.61; N, 2.13; Ge, 27.95%. Yield 0.42 g (21%).



$\text{PhGe}(\text{OMe})_3$ (1.20 g; 4.9 mmol) in 60 ml of an ethanol/methanol (1:1) solution was mixed with solid Na (0.14 g; 5.9 mmol). Mixture was heated under reflux for 2 h. Afterwards, the solution was cooled to room temperature and 0.40 g (3.0 mmol) of anhydrous CuCl_2 was added at once. The solution was left under stirring overnight and 0.15 g (0.9 mmol) of 2,2'-bipyridine were added. Resulted mixture was left under stirring for 4 h and then filtered from the insoluble part. The filtrate was stored in a warm place in a flask equipped by septum with two needles to admit a slow current of nitrogen and evaporation of the solvents. After approximately 7 days the formation of crystalline material **2** was occurred; a few selected single crystals were used for the X-ray diffraction analysis (see ESI for details). Anal. Calcd for $[(\text{PhGeO}_{1.5})_{10}(\text{CuO})_6(\text{HO}_{0.5})_2(\text{C}_{10}\text{H}_8\text{N}_2)_2]$ Cu, 14.98; N, 2.20; Ge, 28.54. Found (for vacuum-dried sample): Cu, 14.89; N, 2.14; Ge, 28.35%. Yield 0.78 g (39%).



$\text{PhGe}(\text{OMe})_3$ (1.20 g; 4.9 mmol) in 60 ml of an ethanol/methanol (1:1) solution was mixed with solid Na (0.14 g; 5.9 mmol). Mixture was heated under reflux for 2 h. Afterwards, the solution was cooled to room temperature and 0.40 g (3.0 mmol) of anhydrous CuCl_2 was added at once. The solution was left under stirring overnight and 0.15 g (0.9 mmol) of 1,10-phenanthroline were added. Resulted mixture was left under stirring for 4 h and then filtered from the insoluble part. The filtrate was stored in a warm place in a flask equipped by septum with two needles to admit a slow current of nitrogen and evaporation of the solvents. After approximately 7 days the formation of crystalline material **3** was occurred; a few selected single crystals were used for the X-ray diffraction analysis (see ESI for details). Anal. Calcd for $[(\text{PhGeO}_{1.5})_{10}(\text{CuO})_6(\text{CH}_3\text{O}_{0.5})_2(\text{C}_{12}\text{H}_8\text{N}_2)_2]$ Cu, 14.55; N, 2.14; Ge, 27.71. Found (for vacuum-dried sample): Cu, 14.40; N, 2.09; Ge, 27.59%. Yield 0.30 g (15%).



PhGe(OMe)₃ (1.20 g; 4.9 mmol) in 14 ml of an ethanol/methanol (1:1) solution was mixed with solid Na (0.14 g; 5.9 mmol). Mixture was heated under reflux for 2 h. Afterwards, the solution was cooled to room temperature and 0.40 g (3.0 mmol) of anhydrous CuCl₂, dissolved in 55 ml of DMF, was added at once. The solution was left under stirring overnight and 0.15 g (0.9 mmol) of 1,10-phenanthroline were added. Resulted mixture was left under stirring for 4 h and then filtered from the insoluble part. The filtrate was stored in a warm place in a flask equipped by septum with two needles to admit a slow current of nitrogen and evaporation of the solvents. After approximately 7 days the formation of crystalline material **4** was occurred; a few selected single crystals were used for the X-ray diffraction analysis (see ESI for details). Anal. Calcd for [(PhGeO_{1.5})₁₀(CuO)₆(HO_{0.5})_{1.6}(C₂H₅O_{0.5})_{0.4}(C₁₂H₈N₂)₂] Cu, 14.64; N, 2.15; Ge, 27.89. Found (for vacuum-dried sample): Cu, 14.61; N, 2.11; Ge, 27.81%. Yield 0.64 g (31%).

[(PhGeO_{1.5})₁₀(CuO)₆(HCOO_{0.5})₂(C₁₂H₈N₂)₂][MeOH] (**5**)

PhGe(OMe)₃ (1.20 g; 4.9 mmol) in 60 ml of an ethanol/methanol (1:1) solution was mixed with solid Na (0.14 g; 5.9 mmol). Mixture was heated under reflux for 2 h. Afterwards, the solution was cooled to room temperature and 0.40 g (3.0 mmol) of anhydrous CuCl₂ was added at once. The solution was left under stirring overnight and 0.15 g (0.9 mmol) of 1,10-phenanthroline were added. Resulted mixture was left under stirring for 4 h and then filtered from the insoluble part. The filtrate was stored in a warm place in a flask with contact to atmosphere to let slow evaporation of the solvents. After approximately two weeks the formation of crystalline material **5** was occurred; a few selected single crystals were used for the X-ray diffraction analysis (see ESI for details). Anal. Calcd for [(PhGeO_{1.5})₁₀(CuO)₆(HCOO_{0.5})₂(C₁₂H₈N₂)₂] Cu, 14.39; N, 2.12; Ge, 27.42. Found (for vacuum-dried sample): Cu, 14.30; N, 2.08; Ge, 27.31%. Yield 0.29 g (14%).

[(PhGeO_{1.5})₁₀(CuO)₆(CH₃COO_{0.5})₂(C₁₀H₈N₂)₂][MeOH]_{0.5} (**6**)

PhGe(OMe)₃ (1.20 g; 4.9 mmol) in 60 ml of an ethanol/methanol (1:1) solution was mixed with solid Na (0.14 g; 5.9 mmol). Mixture was heated under reflux for 2 h. Afterwards, the solution was cooled to room temperature and 0.40 g (3.0 mmol) of anhydrous CuCl₂ was added at once. The solution was left under stirring overnight and 0.18 g (0.9 mmol) of 2,2'-bipyridine were added. Resulted mixture was left under stirring for 4 h and then filtered from the insoluble part. The filtrate was stored in a warm place in a flask with contact to atmosphere to let slow evaporation of the solvents. After approximately two weeks the formation of crystalline

material **6** was occurred; a few selected single crystals were used for the X-ray diffraction analysis (see ESI for details). Anal. Calcd for $[(\text{PhGeO}_{1.5})_{10}(\text{CuO})_6(\text{CH}_3\text{OO}_{0.5})_2(\text{C}_{10}\text{H}_8\text{N}_2)_2] \text{Cu}$, 14.50; N, 2.13; Ge, 27.63. Found (for vacuum-dried sample): Cu, 14.42; N, 2.09; Ge, 27.54%. Yield 0.23 g (11%).

Hydroperoxidation of Alkanes by Hydrogen Peroxides

Catalyst **1** or **2** was introduced into the reaction mixture in the form of solid powder. The alkane was then added and the reaction started when hydrogen peroxide was introduced in one portion. (**CAUTION.** The combination of air or molecular oxygen and H_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 made previously, the samples obtained in the alkane oxidation were typically analyzed twice (before and after their treatment with PPh_3) by GC. The chromatograph-3700 (fused silica capillary column FFAP/OV-101 20/80 w/w, $30 \text{ m} \times 0.2 \text{ mm} \times 0.3 \mu\text{m}$; helium as a carrier gas was employed. The method of comparison of chromatograms of the same sample obtained before and after addition of PPh_3 which was proposed by Shul'pin earlier [109-118] allowed us to estimate 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. Blank experiments with cyclohexane showed that in the absence of a catalyst products were formed in negligible concentrations.

Oxidation of Alcohols to Ketones by TBHP

These reactions were carried out analogously. Triphenylphosphine was added in order to reduce remain TBHP to *tert*-butanol. The reactions with 1-phenylethanol were analyzed by ^1H NMR method (solutions in acetone- d_6 ; "Bruker AMX-400" instrument, 400 MHz).

Oxidation of Alcohols and Amines into Amides

In a sealed tube were added successively amine hydrochloride (0.5 mmol), CaCO_3 (50.1 mg, 0.5 mmol), CH_3CN (1mL), **2** (0.9 mg, 0.002 mmol, 0.2 mol% in Cu), benzylic alcohol (105 μL , 1.0 mmol) and TBHP (5.5M in nonane, 225 μL , 1.25mmol). The mixture was stirred at 80°C for 2h and TBHP (5.5M in nonane, 225 μL , 1.25mmol) were again added to the mixture. After 22h at 80°C , the mixture was cooled to room temperature and 1N HCl and EtOAc were added. The mixture was extracted twice with EtOAc, and the combined organic phases were washed with a saturated solution of NaHCO_3 and brine, and concentrated under reduced pressure. To remove the excess of benzylic alcohol, 80 mL of H_2O were added and evaporated under reduced pressure. Crude product was then purified using silica

gel chromatography using gradients of cyclohexane/EtOAc to yield the pure compounds. Purity of amides was confirmed by ^1H and ^{13}C NMR analysis and comparison with literature data.

Conclusions

Here we presented that simple self-assembling reaction (starting from $\text{PhGe}\{\text{OMe}\}_3$) could be an effective instrument for the synthesis of cage-like Cu(II)-based phenylgermsesquioxanes, containing N,N-ligands of 2,2'-bipyridine family. Similar composition of all six isolated products, with the same ratio of "key elements", namely Ge/Cu/N = 10/6/4, pointed out to an increased stability of this type of molecular geometry. Additional ligation of cage complexes **1-6** came from OX species ($\text{X} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, \text{HCO}, \text{CH}_3\text{CO}$). Among these, especial interest is attracted by formate and acetate fragments, formed due to spontaneous oxidation of corresponding alcohols (MeOH and EtOH), used as reaction media.

Proneness to oxidation activity of Cu-germsesquioxane was indeed confirmed by catalytic tests, used as precatalysts. This investigation demonstrated that compounds **1** and **2** are efficient catalysts in the oxidation of alkanes, benzene and alcohols with hydroperoxides. Additionally, complex **2** was also highly efficient in the formation of amides from alcohols and amines. Further studies of cage metallacomplexes (based on germanium sesquioxanes) and their catalytic properties are currently on their way in our teams.

Conflicts of interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary data related to this article (details of X-ray experiments, Table S1) can be found at [https:// doi.org/...xxxx](https://doi.org/...xxxx)

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