Palanquin-Like Cu$_4$Na$_4$ Silsesquioxane Synthesis (via Oxidation of 1,1-bis(Diphenylphosphino)methane), Structure and Catalytic Activity in Alkane or Alcohol Oxidation with Peroxides

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Abstract: The self-assembly synthesis of copper-sodium phenylsilsesquioxane in the presence of 1,1-bis(diphenylphosphino)methane (dppm) results in an unprecedented cage-like product: $[(PhSiO_{1.5})_6]_2[CuO]_4[NaO_{0.5}]_4[dppmO_2]_2$ **1**. The most intriguing feature of the complex **1** is the presence of two oxidized dppm species that act as additional O-ligands for sodium ions. Two cyclic phenylsiloxanolate $(PhSiO_{1.5})_6$ ligands coordinate in a sandwich manner with the copper(II)-containing layer of the cage. The structure of **1** was established by X-ray diffraction analysis. Complex **1** was shown to be a very good catalyst in the oxidation of alkanes and alcohols with hydrogen peroxide or *tert*-butyl hydroperoxide in acetonitrile solution. Thus, cyclohexane (CyH), was transformed into cyclohexyl hydroperoxide (CyOOH), which could be easily reduced by PPh$_3$ to afford stable cyclohexanol with a yield of 26% (turnover number (TON) = 240) based on the starting cyclohexane. 1-Phenylethanol was oxidized by *tert*-butyl hydroperoxide to give acetophenone in an almost quantitative yield. The selectivity parameters of the oxidation of normal and branched alkanes led to the conclusion that the peroxides H$_2$O$_2$ and *tert*-BuOOH, under the action of compound (**1**), decompose to generate the radicals HO$^\bullet$ and *tert*-BuO$^\bullet$ which attack the C-H bonds of the substrate.

Keywords: alkanes; hydrogen peroxide; copper complexes; metallasilsesquioxanes; dppm oxidation

1. Introduction

Cage metallasilsesquioxanes (CLMSs) [1–10] are popular objects for the investigation of regularities in the insertion of metal ions into the siloxane matrix [11–18], the study of catalytic [19–24]

properties, magnetic (spin) glass [25], as well as the study of nanoparticles [26] and macrocyclic siloxane material [27] formation.

Among the synthetic approaches to cage metallasilsesquioxanes, the one based on the involvement of additional organic ligands has attracted significant attention due to the formation of extravagant molecular architectures, (e.g., [12,28–32]). In the continuation of these works, our team has recently suggested that the simplest method of the "mixed ligand synthesis" of CLMSs is to introduce additional organic ligand into the reaction mixture before the formation of the cage product. A modified self-assembly procedure such as this in most cases leads to the "ligand synergy" situation, with different ligands coordinating metal ions of the same cage compound. This feature was observed for several types on N-based ligands: 1,10-phenanthroline [33,34], 2,2′-bipyridine [33–35], and bathophenantroline [34–36]. Dual behavior was detected for the neocuproine-assisted synthesis of Cu(II)-CLMS: in the case of DMF/dioxane reaction/crystallization media, a similar "ligand synergy product" was formed [37], while DMF media favors the isolation of "ligand antagonism" product with the redistribution of copper centers between silsesquioxane and neocuproine ligands [38], as seen in Figure 1. This particular antagonistic behavior was also found in the P-ligand-assisted self-assembly of Cu-CLMSs; this reaction was found to be tuned with two types of product being available for the reaction with 1,2-bis(diphenylphosphino)ethane [39], as seen in Figure 2.
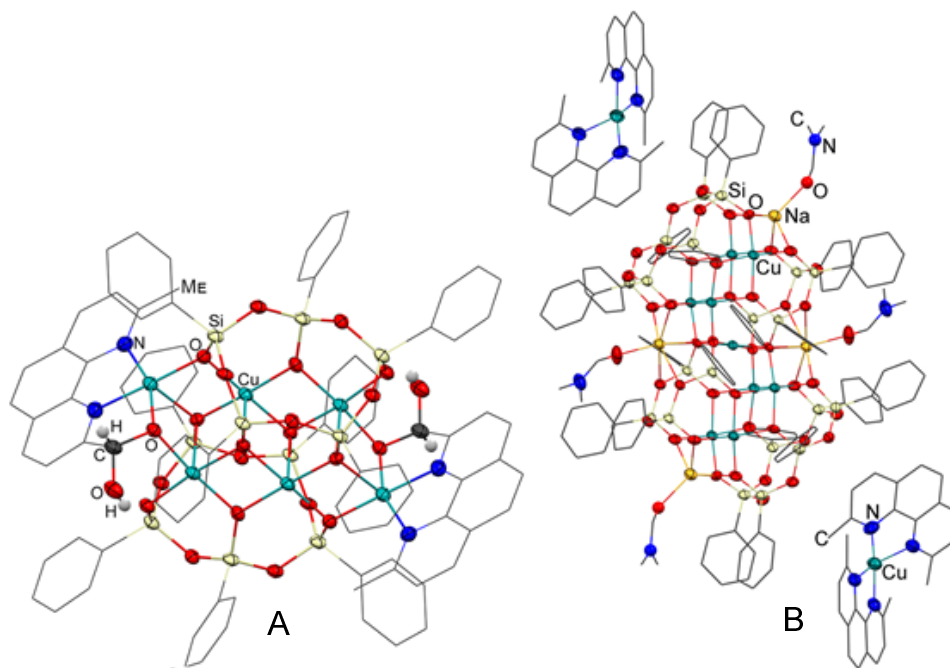

Figure 1. Features of cage Cu-CLMSs' interaction with *N,N*-ligand (neocuproine). **Left**: Compound **A** with silsesquioxane and neocuproine ligands as parts of the same unit (Ref. [37]). **Right**: Ionic complex **B** with copper ions redistributed between silsesquioxane and neocuproine ligands (Ref. [38]). CLMS: cage metallasilsesquioxanes.

In the present article, we obtained non-trivial results from the synthesis with a close analogue of 1,2-bis(diphenylphosphino)ethane, namely, 1,1-bis(diphenylphosphino)methane (dppm). In the present article, we obtained non-trivial results from the synthesis with a close analogue of 1,2-bis(diphenylphosphino)ethane, namely, 1,1-bis(diphenylphosphino)methane (dppm). To our delight, the self-assembly reaction of $[(PhSiO_{1.5})(NaO_{0.5})]n$ (obtained in situ from $PhSi(OEt)_3$) with $CuCl_2$ in the presence of dppm resulted in the isolation (in a 22% yield) of heterometallic (Cu_4/Na_4) cage-like phenylsilsesquioxane **1**, as seen in Scheme 1.

Figure 2. Ionic complexes with copper ions redistributed between silsesquioxane and 1,2-bis(diphenylphosphino)ethane ligands (Ref. [39]). **Left**: Compound **C** with four copper(II) ions in the cage unit. **Right**: Compound **D** with nine copper(II) ions in the cage unit.

Scheme 1. The synthesis of $[(PhSiO_{1,5})_6]_2[CuO]_4[NaO_{0.5}]_4[dppmO_2]_2$ (complex **1**) during the self-assembly reaction of $[(PhSiO_{1.5})(NaO_{0.5})]_n$ with $CuCl_2$, assisted by the (in situ oxidized) dppm ligand.

The structure of **1** was established by an X-ray diffraction study, as seen in Figure 3 (see also ESI results). This study found that the formation of **1** was indeed accompanied by dppm ligands. Surprisingly, the way that dppm was found to act, is principally different to earlier mentions of dppe activity. Namely, dppm underwent in situ oxidation into its dioxide, dppmO$_2$, followed by the coordination to sodium ions. It is important to note that the oxidation of dppm to dppmO$_2$ was previously reported in the literature [40]. Moreover, some examples of oxidations during CLMS synthesis were described [33,34,37,41–45], but to the best of our knowledge, no single example of CLMS synthesis accompanied by dppm oxidation has been reported to date. An additional and intriguing feature of such oxidation that acted favorably in aiding the formation of **1** is the requirement of mild conditions. In this respect, we would like to suggest the influence of copper ions as catalytic centers and the presence of trace oxygen as an oxidant.
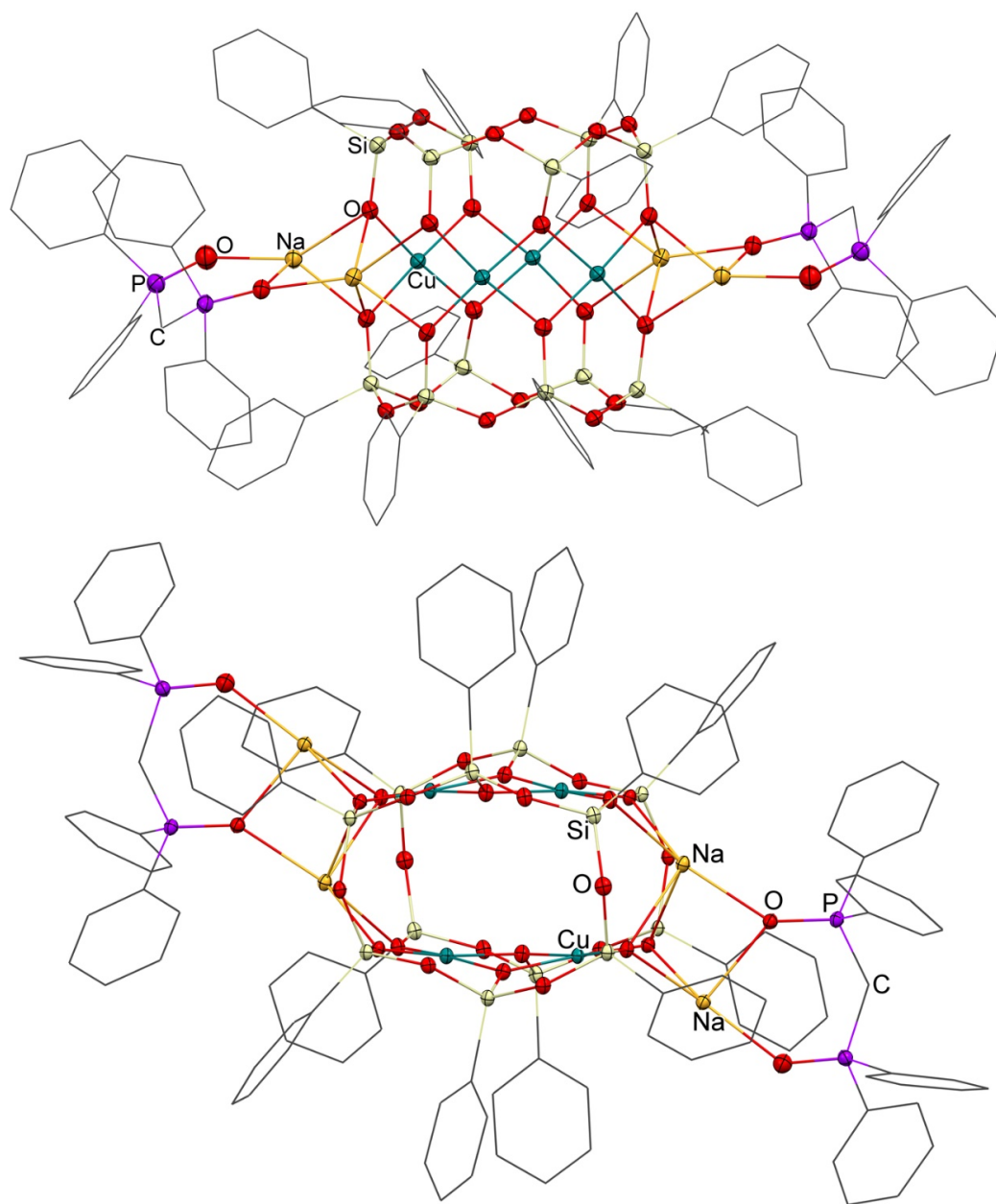

Figure 3. The molecular structure of **1**. **Top**: Front view. **Bottom**: Top view. Color code: copper—green, sodium—yellow, oxygen—red, phosphorous—purple.

Regarding the rest of the structure of **1**, it is also notable that the principle of cyclic silsesquioxane ligands' coordination to copper ions (in a sandwich manner as seen in Figure 4, left) is well-described in CLMSs chemistry [1,6,10]. In turn, the location of sodium ions in **1** is far from being classical. For a regular structure of sandwich CLMS, including four alkaline metal ions (e.g., Ref. [45]), it is quite easy to distinguish two pairs of alkaline metal ions (in axial and equatorial positions, respectively, as seen in Figure 4, center). In contrast to this, all of the sodium ions in **1** lay in equatorial positions, which allow for each dppmO$_2$ species to coordinate two sodium centers, as seen in Figure 4, right. Such coordination provokes a deep distortion of the sandwich skeletons of **1**, in comparison with similar fragments described in Refs. [39] (as seen in Figure 1) and [45] (as seen in Figure 2, center) (several distances and angles are provided in Table 1). The six-membered Na-dppm (Na-O-P-C-P-O) rings adopt a *sofa* conformation with the carbon atom out of the mean plane, which passed through the other atoms of the ring by 0.737(6) Å, as seen in Figure 3, A. The dihedral angle between the plane of Na,Cu-ions and the basal plane of the six-membered Na-dppm rings is 13.64(10)°. Additional crystallographic information is provided in the ESI (Tables S1–S6).
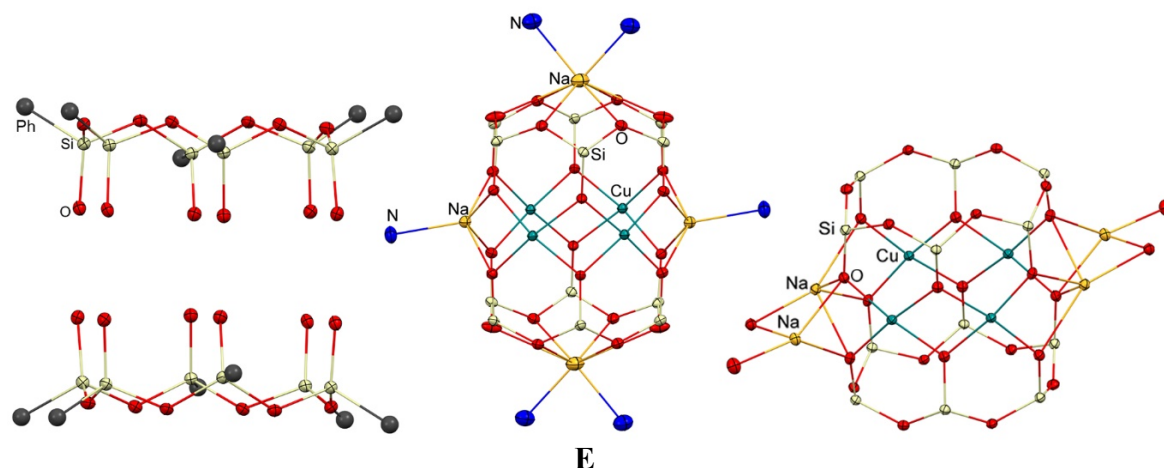

Figure 4. Left: Structure of silsesquioxane ligands in **1**. **Center**: Molecular structure of Cu$_4$-CLMSs from Ref. [45], representing the axial and equatorial locations of sodium centers. **Right**: The framework of **1**, representing equatorial-only locations of sodium centers. Color code: copper—green, sodium—yellow, oxygen—red, nitrogen—blue.

Table 1. Structural comparison of Cu$_4$-based CLMSs.

Compound	The Shortest Distance between Opposing Silicon Atoms in [PhSiO$_{1.5}$]$_6$ Silsesquioxane Ligand, Å
1 (this work)	5.114
C (complex from Ref. [39])	5.584
E (complex from Ref. [45])	5.677

2. Oxidation of Hydrocarbons and Alcohols with Peroxides

Complexes of transition metals are known to catalyze the oxidation of hydrocarbons and alcohols with peroxides [46–50]. In the present work, we found that complex **1** exhibited catalytic activity in the oxidation of cyclohexane and other alkanes with H$_2$O$_2$ in acetonitrile, in the presence of nitric acid. Catalysts of this type have been shown to exhibit high catalytic activity. It was interesting to introduce phosphorus atoms into the catalyst structure.

The experiment shown in Figure 5 demonstrated that the reduction of the reaction solution with PPh$_3$ gave rise to a higher concentration of cyclohexanol and a decrease of cyclohexanone concentration (compare top and bottom graphs in Figure 5). These changes testify that the alkyl hydroperoxide was formed in the course of the oxidation (the so called Shul'pin method [51–64]).
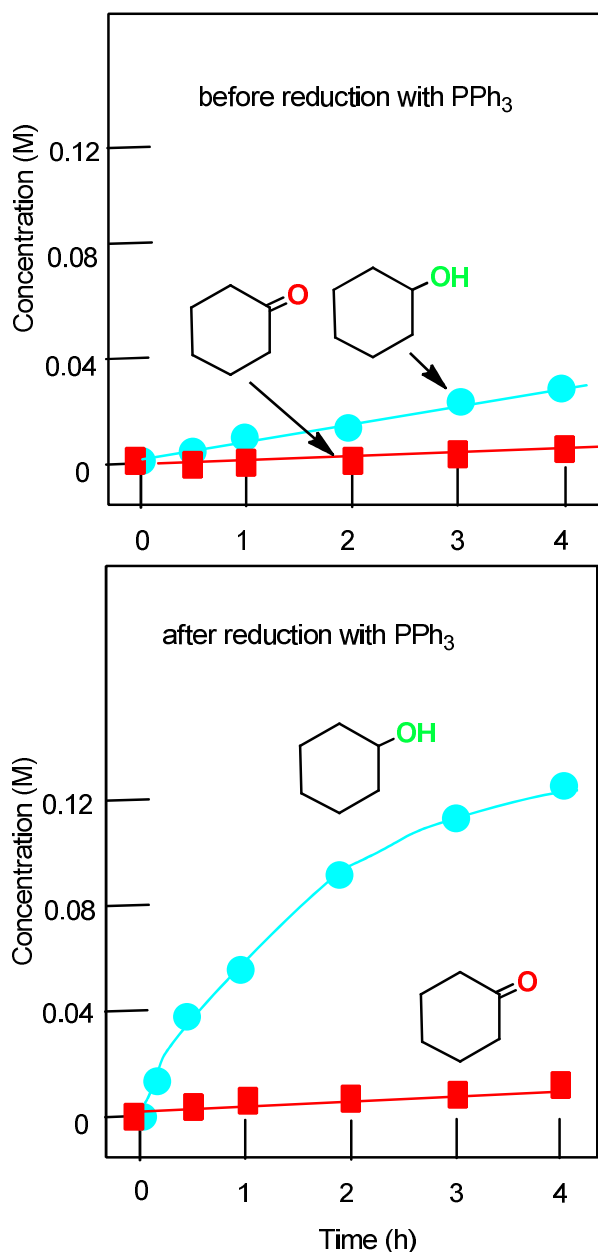
Figure 5. The accumulation of cyclohexanol and cyclohexanone in the oxidation of cyclohexane (0.46 M) with H_2O_2 (2 M) catalyzed by complex **1** (5×10^{-4} M), in the presence of HNO_3 (0.05 M) at 50 °C. In order to detect the formation of cyclohexyl hydroperoxide, the concentrations of the products were measured by GC before and after the reduction of the reaction sample with solid PPh_3. In the absence of HNO_3, the oxidation afforded only 0.015 M of products after 2 h (after the reduction of the reaction sample with solid PPh_3).

The following selectivity parameters were obtained for the oxidation of *n*-heptane: C(1):C(2):C(3):C(4) = 1.0:5.3:5.6:5.0 (after 1 h) and 1.0:6.1:5.8:5.8 (after 3 h); of methylcyclohexane: 1°:2°:3° = 1.0:5.4:15.0; and of *cis*-1,2-dimethylcychohexane: t/c = 0.8 (the last parameter means that the *trans/cis* ratio of produced corresponding isomeric tertiary alcohols was 0.8). The character of dependence of the initial cyclohexane oxidation rate on the initial hydrocarbon concentration (approaching a plateau at [cyclohexane]$_0$ ~0.3 M; Figure 6), as well as the selectivity parameters measured here, indicate that the reaction occurred with the participation of hydroxyl radicals, and alkyl hydroperoxides were formed as the main primary products [65].We assumed that added nitric acid induced the transformation of the catalyst into an active form.
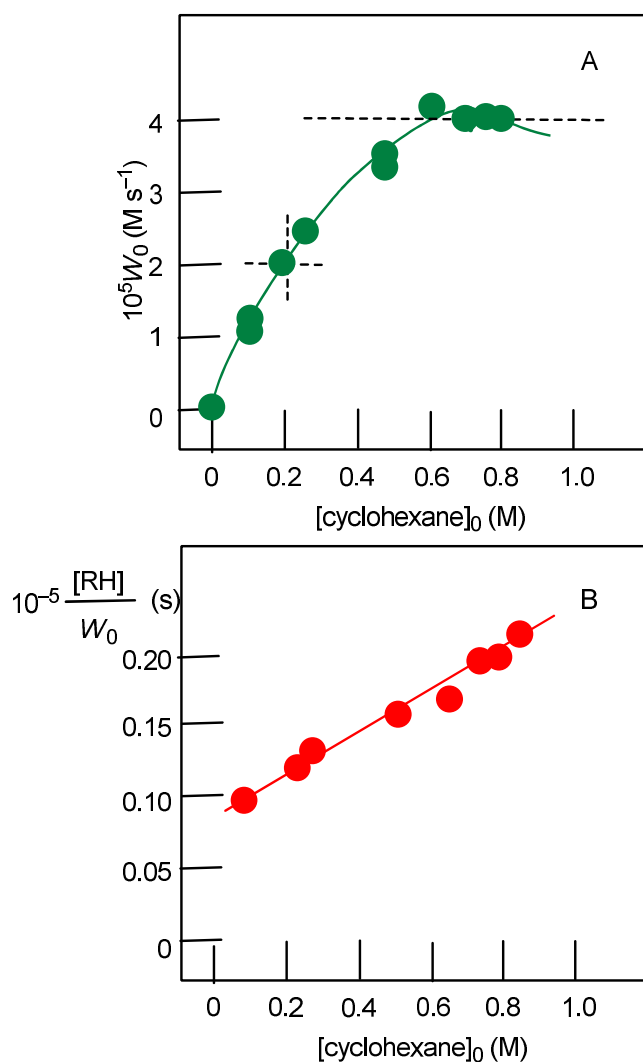
Figure 6. The dependence of the oxidation rate W_0 on the initial concentration of cyclohexane in the oxidation of cyclohexane into cyclohexanol and cyclohexanone (a sum) with H_2O_2 (2.0 M) catalyzed by complex **1** in the presence of HNO_3 (0.05 M). Conditions: catalyst **1** (5×10^{-4} M), 50 °C, concentrations of products were measured by GC only after the reduction of the reaction sample with solid PPh_3. Linearisation of the curve shown in Graph **A** is presented in Graph **B**.

The dependence of the reaction rate on the temperature of the reaction solution obeys the Arrhenius law, which allowed us to measure the effective activation energy (see Figure 7). The activation energy of cyclohexane oxidation was equal to 13.6 kcal/mol. The main increment of this value was from the process of catalytic H_2O_2 decomposition, which generated species inducing cyclohexane oxidation.

Complex **1** was found to efficiently catalyze the transformation of alcohols into the corresponding ketones by the oxidation with *tert*-butyl hydroperoxide, as seen in Figure 8.

The data presented in Figure 8 demonstrate that in the presence of complex **1** and *tert*-Bu-OOH, 1-phenylethanol was oxidized more effectively in comparison with cyclohexanol and heptanol-2. The characteristic times of the kinetic curves of the formation of corresponding ketones in the case that three alcohols were similar and that the maximum concentration of ketones including acetophenone was achieved when *tert*-Bu-OOH was completely diseased. Thus, the *tert*-Bu-OOH decomposition rates in the presence of three alcohols were similar and the active species generation rates for all alcohols were the same. The lower yields of ketones in comparison with the initial TBHP concentration were due to the concurrent reaction of TBHP with acetonitrile. 1-Phenyethanol exhibited a higher

reactivity in comparison with two other alcohols. This result was in accord with the known information regarding the higher constant that comes from the reaction of aromatic alcohols with hydroxyl radicals in comparison with constants measured for aliphatic alcohols [65].
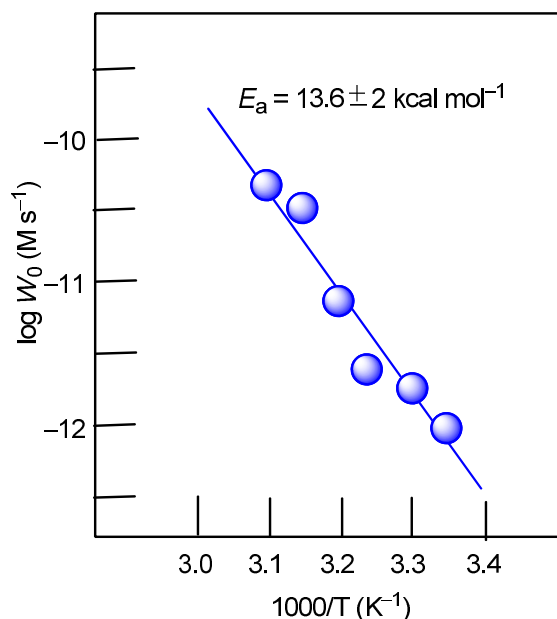

Figure 7. The Arrhenius plot of the oxidation of cyclohexane (0.46 M) with H_2O_2 (50%, 2 M), catalyzed by compound **1** (5×10^{-4} M) in acetonitrile, in the presence of HNO_3 (0.05 M). Concentrations of products were measured by GC after the reduction of the reaction sample with solid PPh_3.
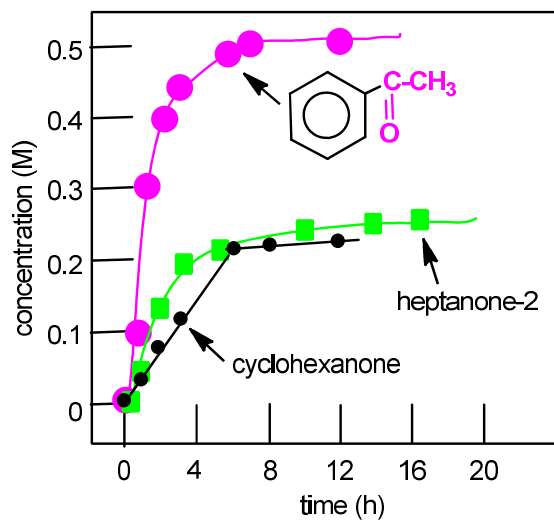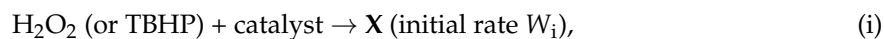

Figure 8. Accumulation of cyclohexanone, heptanone-2, and acetophenone in the oxidation of cyclohexanol (0.46 M), heptanol-2 (0.42 M), or 1-phenylethanol (0.5 M), respectively, with *tert*-butyl hydroperoxide (1.5 M) catalyzed by complex **1** (5×10^{-4} M) in the absence of HNO_3 at 50 °C. In order to quench the oxidation process, concentrations of products were measured by GC only after the reduction of the reaction sample with solid PPh_3.

The dependence of the initial 1-phenylethanol (ROH) oxidation rates by TBHP, as seen in Figure 9, on the initial ROH concentration was in accordance with an assumption on the oxidation of ROH by intermediate species generated in the catalytic peroxide decomposition. This species, **X**, reacts in two parallel routes with ROH and the solvent CH_3CN. Let us consider the following kinetic scheme:

$$H_2O_2 \text{ (or TBHP)} + \text{catalyst} \rightarrow \textbf{X} \text{ (initial rate } W_i\text{)}, \tag{i}$$

$$ROH + \textbf{X} \rightarrow R_1O^\bullet, \tag{1}$$

$$CH_3CN + \textbf{X} \rightarrow \text{products}. \tag{2}$$

Here, stage (i) reflects the process of the generation of **X** with the rate W_i; stages (1) and (2) are from the processes of the interaction of **X** with ROH and CH_3CN, respectively, with the constants k_1 and k_2. In the frames of quasi-stationary estimation, we can obtain the following equation for the initial rate of $RO^\bullet$ generation:

$$(d[R_1O^\bullet]/dt)_0 = W_i/(1 + k_2[CH_3CN]/k_1[ROH]_0). \tag{3}$$

Analysis of the experimental data shown in Figures 6 and 9 in accordance with Equation (3) allowed us to determine the values of $k_2[CH_3CN]/k_1$ for the oxidation of ROH by hydrogen peroxide (0.44 M) and TBHP (0.33 M), respectively. These parameters were distinguished from the values typical for hydroxyl radicals (~0.1 M). However, the parameters of selectivity (see above) indicated that hydroxyl radicals took part in the oxidation with hydrogen peroxide. It is not yet clear what the reason for this discrepancy is, and this will be the subject of further research.
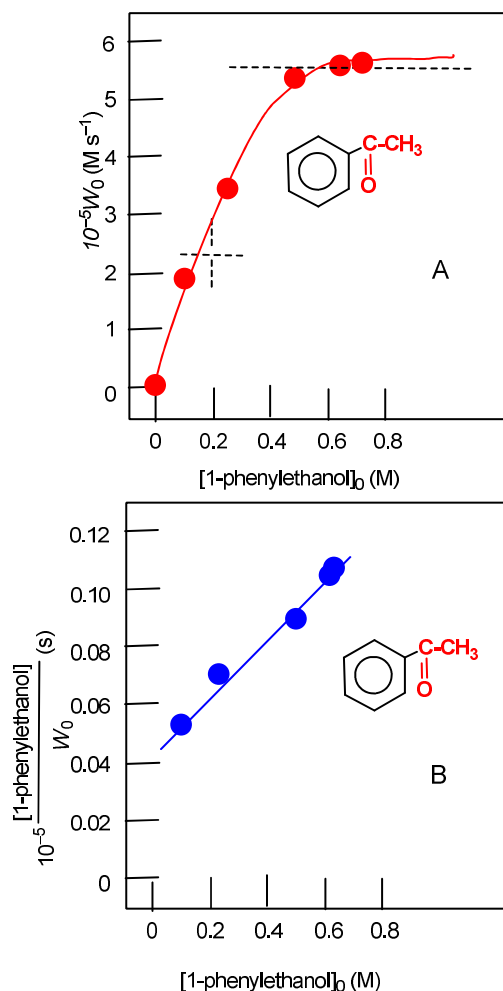

Figure 9. The dependence of the initial oxidation rate W_0 on the initial concentration of 1-phenylethanol in its oxidation into acetophenone with *tert*-butyl hydroperoxide (1.5 M) catalyzed by complex **1** (5 × 10^{-4} M), 50 °C. Concentrations of products were measured by GC only after the reduction of the reaction sample with solid PPh_3 in order to quench the oxidation process. Linearization of the curve, as shown in Graph **A**, is presented in Graph **B**.

3. Conclusions

The oxidation of 1,1-bis(diphenylphosphino)methane to its dioxide, under mild conditions, favored the formation of the unusual heterometallic cage silsesquioxane $[(PhSiO_{1.5})_6]_2[CuO]_4[NaO_{0.5}]_4[dppmO_2]_2$. The copper ions of the product were coordinated in a sandwich manner by two cyclic $(PhSiO_{1.5})_6$ ligands. In turn, sodium ions of the complex were located in the external positions and were ligated by both silsesquioxane species and $dppmO_2$ species. Such "oxidative activity" was additionally confirmed by catalytic tests. Cyclohexane, CyH, was transformed into cyclohexyl hydroperoxide CyOOH, which could be easily reduced by PPh_3 to afford stable cyclohexanol. 1-Phenylethanol was oxidized by *tert*-butyl hydroperoxide to give acetophenone in an almost quantitative yield. The selectivity parameters of oxidation of normal and branched alkanes led to the conclusion that peroxides H_2O_2 and *tert*-BuOOH under the action of compound **1** decomposed to generate the radicals $HO^\bullet$ and *tert*-$BuO^\bullet$, which attacked the C-H bonds of the substrate.

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