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# Heptanuclear Fe<sub>5</sub>Cu<sub>2</sub>-Phenylgermsesquioxane containing 2,2'-Bipyridine: Synthesis, Structure, and Catalytic Activity in Oxidation of C–H Compounds

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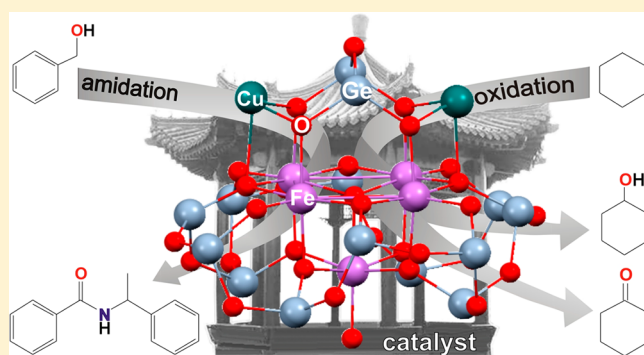
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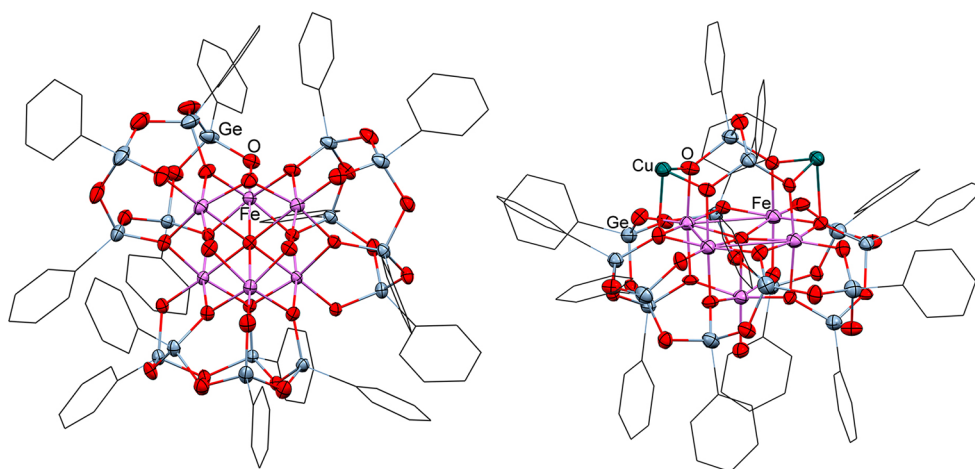
**ABSTRACT:** A new representative of an unusual family of metallagermaniums sesquioxanes, namely the heterometallic cage-like phenylgermsesquioxane (PhGeO<sub>2</sub>)<sub>12</sub>Cu<sub>2</sub>Fe<sub>5</sub>(O)OH-(PhGe)<sub>2</sub>O<sub>5</sub>(bipy)<sub>2</sub> (**2**), was synthesized and structurally characterized. Fe(III) ions of the complex are coordinated by oxa ligands: (i) cyclic (PhGeO<sub>2</sub>)<sub>12</sub> and acyclic (Ph<sub>2</sub>Ge<sub>2</sub>O<sub>5</sub>) germoxanولات and (ii) O<sup>2-</sup> and (iii) HO<sup>-</sup> moieties. In turn, Cu(II) ions are coordinated by both oxa (germoxanولات) and aza ligands (2,2'-bipyridines). This "hetero-type" of ligation gives in sum an attractive pagoda-like molecular architecture of the complex **2**. Product **2** showed a high catalytic activity in the oxidation of alkanes to the corresponding alkyl hydroperoxides (in yields up to 30%) and alcohols (in yields up to 100%) and in the oxidative formation of benzamides from alcohols (catalyst loading down to 0.4 mol % in Cu/Fe).



## INTRODUCTION

The design of metal-based 3D (polycyclic, cage-like) compounds has been the focus of numerous research teams worldwide due to their structural multiplicity and varied potential applications.<sup>1</sup> Among cage metalla complexes, a significant amount of attention has been given to metallasilsesquioxanes—metalla derivatives of silicon sesquioxane (RSiO<sub>1.5</sub>) cage compounds. The major features of these compounds are (i) high flexibility of silsesquioxane ligands, permitting a great number of structures and (ii) a universality of these ligands, readily complexing to a wide range of metal ions.<sup>2</sup> In turn, cage-like metallasilsesquioxanes based on germanium instead of silicon (metallagermsesquioxanes) are quite rare. A hydrothermal synthetic approach to "hybrid" metallagermsesquioxanes, including metal ions in the composition of both metallagermoxane units M–O–Ge and carboxylic acid salt fragments –COOM, was first reported by Yang and co-workers in 2009.<sup>3</sup> Lately, this synthetic procedure has been elaborated in several additional works.<sup>4</sup> An alternative method of synthesis, which allowed isolation of the first

example of cage compounds, constructed solely from metallagermoxane units M–O–Ge, has been suggested by some of us in recent work.<sup>5</sup> This approach, employing the self-assembling reaction of PhGe(OMe)<sub>3</sub> with Na<sup>+</sup> and Fe<sup>3+</sup> cations, leads to the formation of the unusual three-pointed-star geometry [(Ph<sub>3</sub>Ge<sub>5</sub>O<sub>10</sub>)<sub>3</sub>Fe<sub>6</sub>(OH)<sub>3</sub>(O)Na<sub>2</sub>]·2EtOH·H<sub>2</sub>O (**1**) with an Fe<sub>6</sub>O<sub>19</sub> "Lindqvist ion" central unit, surrounded by three germoxanolate [PhGeO<sub>1.5</sub>]<sub>5</sub> ligands (Figure 1, left). This particular architecture allows the observation of magnetic interactions of Fe ions as well as high catalytic activity. Here we present the progress of metallagermsesquioxane chemistry—the opportunity to synthesize cage germesquioxane, incorporating different types of transition-metal ions. Along with their fundamental interest, such multimetallic compounds are known to be extremely effective in catalysis.<sup>6</sup> Among these, mixed Fe/Cu complexes were proved to be active in a wide range of relevant processes, e.g. in Fischer–Tropsch synthesis,<sup>7</sup> the



**Figure 1.** Simplified view of (left) Fe,Na-phenylgermsesquioxane **1**<sup>5</sup> and (right) Fe,Cu-phenylgermsesquioxane **2** (bipy ligands are omitted for clarity). Color code: Ge, gray; O, red; Fe, lilac; Cu, green.

water-gas shift reaction,<sup>8</sup> semihydrogenation of alkynes,<sup>9</sup> CO<sub>2</sub> reduction,<sup>10</sup> C–H borylation,<sup>11</sup> small-molecule activation,<sup>12</sup> and carbon–carbon and carbon–heteroatom coupling reactions.<sup>13</sup> Keeping in mind the prominent metallic character of germanium itself, one could expect a high catalytic activity of Cu/Fe/Ge complexes. In accord with this, we were interested in the synthesis of mixed Fe/Cu germsesquioxanes and the application of such products in catalysis. Here we present the first example of the Fe(III)/Cu(II) phenylgermsesquioxane **2** (Figure 1, right) and the study of this compound catalytic activity.

## EXPERIMENTAL SECTION

**Materials.** Phenyltrimethoxygermane (ABCR) and other chemicals (Sigma-Aldrich) were used without further purification. Methanol was distilled prior to use following a trivial procedure.

The Fe,Na-phenylgermsesquioxane [(Ph<sub>3</sub>Ge<sub>5</sub>O<sub>10</sub>)<sub>3</sub>Fe<sub>6</sub>(OH)<sub>3</sub>(O–Na)<sub>2</sub>·2EtOH·H<sub>2</sub>O (**1**) was synthesized as described in ref 5.

**Synthesis of Complex 2. Method A.** To a methanol/toluene (50 mL/15 mL, placed in a round-bottom flask) solution were added compound **1** (0.300 g, 0.09 mmol) and, after total dissolution of **1**, copper(II) chloride (0.012 g, 0.09 mmol). The mixture was rigorously stirred for 3 h. Then 2,2'-bipyridine (0.014 g, 0.09 mmol) was added at once to the solution and the resulting mixture was stirred overnight. Filtration of the mixture from the insoluble part gave a clear solution, suitable for crystallization. Slow evaporation of the solvents over 2 weeks gave a crystalline material. Several crystals were used for the single-crystal X-ray diffraction analysis (see below for details). Anal. Calcd for {[Fe<sub>5</sub>O<sub>17</sub>(OH)]Cu<sub>2</sub>(bipy)<sub>2</sub>(PhGeO)<sub>12</sub>(PhGe)<sub>2</sub>O}: Ge, 30.70; Fe, 8.43; Cu, 3.84; N, 1.69. Found (for vacuum-dried sample): Ge, 30.53; Fe, 8.32; Cu, 3.76; N, 1.60. Yield: 0.013 g (9%).

**Method B.** PhGe(OMe)<sub>3</sub> (2.00 g, 8.2 mmol) was dissolved in 50 mL of methanol. Then 0.44 g (11.1 mmol) of NaOH was added, and the resulting mixture was heated to reflux for 2 h. Afterward the solution was cooled to room temperature, and 0.48 g (3.00 mmol) of FeCl<sub>3</sub> and 0.16 g (1.17 mmol) of CuCl<sub>2</sub> were added at once. The solution was stirred for 3 h, and then 0.18 g (1.17 mol) of bipy was added at once to the solution and the resulting mixture was stirred overnight. Filtration of the mixture from the insoluble part gave a clear solution, suitable for crystallization. Slow evaporation of solvents over 2 weeks gave a crystalline material. Several crystals were used for the single-crystal X-ray diffraction analysis (cell parameters were found to be equal to those of the product of method A). Anal. Calcd for {[Fe<sub>5</sub>O<sub>17</sub>(OH)]Cu<sub>2</sub>(bipy)<sub>2</sub>(PhGeO)<sub>12</sub>(PhGe)<sub>2</sub>O}: Ge, 30.70; Fe, 8.43; Cu, 3.84; N, 1.69. Found (for vacuum-dried sample): Ge, 30.59; Fe, 8.34; Cu, 3.79; N, 1.61. Yield: 0.40 g (21%).

Elemental analysis was carried out with an XRF VRA-30 spectrometer.

IR spectra were recorded on Shimadzu IR Prestige21 FTIR spectrometer in KBr pellets.

UV–vis absorption spectra were recorded on a Varian Cary 50 spectrophotometer in cells with 5 and 10 mm optical path lengths.

**X-ray Study.** X-ray diffraction data were collected on the “Belok” beamline ( $\lambda = 0.96990$  Å) 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  $\varphi$  scan mode and corrected for absorption using the Scala program.<sup>14</sup> The data were indexed, integrated, and scaled using the utility iMOSFLM in the CCP4 program.<sup>15</sup> For details, see Table S1 in the Supporting Information. The structure was determined by direct methods and refined by full-matrix least-squares techniques on  $F^2$  with anisotropic displacement parameters for non-hydrogen atoms. Six of the twelve phenyl substituents were found to be disordered over two sites with occupancies of 0.50:0.50 or 0.75:0.25. The crystal of **2** contains very large solvent-accessible voids; however, 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.<sup>16</sup> The hydrogen atom of the OH group was localized in the difference Fourier map and included in the refinement within the riding model with fixed isotropic displacement parameters ( $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ ). The other hydrogen atoms were placed in calculated positions and refined within riding model with fixed isotropic displacement parameters ( $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ). All calculations were carried out using the SHELXTL program.<sup>17</sup>

**Oxidation of Alkanes and Alcohols.** The reactions of alcohols and hydrocarbons were carried out in air in thermostated Pyrex cylindrical vessels with vigorous stirring and using MeCN as solvent. Typically, catalyst **2** and the cocatalyst (acid) were introduced into the reaction mixture in the form of stock solutions in acetonitrile. The substrate (alcohol or hydrocarbon) was then added, and the reaction started when hydrogen peroxide or TBHP was introduced in one portion. (**Caution!** The combination of air or molecular oxygen and H<sub>2</sub>O<sub>2</sub> with organic compounds at elevated temperatures may be explosive.) In order to determine concentrations of all cyclohexane oxidation products the samples of reaction solutions after addition of nitromethane as a standard compound were in some cases analyzed twice (before and after their treatment with PPh<sub>3</sub>) by GC (LKhM-80-6 instrument, columns 2 m with 5% Carbowax 1500 on 0.25–0.315 mm Inerton AW-HMDS; carrier gas argon) to measure concentrations of cyclohexanol and cyclohexanone. This method (an excess of solid triphenylphosphine was added to the samples 10–15 min before the GC analysis) was proposed by Shul’pin earlier.<sup>18</sup> Attribution of peaks was made by comparison with chromatograms of authentic samples.

Blank experiments with cyclohexane showed that in the absence of catalyst **2** no products were formed.

**General Procedure for Amidation.** In a sealed tube were added successively amine hydrochloride (0.5 mmol),  $\text{CaCO}_3$  (50.1 mg, 0.5 mmol), anhydrous  $\text{CH}_3\text{CN}$  (1 mL), **2** (0.9 mg, 0.29  $\mu\text{mol}$ ), benzylic alcohol (104  $\mu\text{L}$ , 1.0 mmol), and TBHP (5.5 M in nonane, 225  $\mu\text{L}$ , 1.25 mmol). The mixture was stirred at 80 °C for 2 h, and TBHP (5.5 M in nonane, 225  $\mu\text{L}$ , 1.25 mmol) was again added to the mixture. After 22 h at 80 °C, the mixture was cooled to room temperature and 1 N HCl and AcOEt were added. The mixture was extracted twice with AcOEt, and the combined organic phases were washed with a saturated solution of  $\text{NaHCO}_3$  and brine and concentrated under reduced pressure. To remove the excess of benzylic alcohol, 80 mL of  $\text{H}_2\text{O}$  was added to the organic phase and evaporated under reduced pressure. The crude product was then solubilized in AcOEt, dried over  $\text{MgSO}_4$ , and concentrated under vacuum. The crude product was purified by silica gel chromatography using gradients of cyclohexane/AcOEt to yield the pure compounds.

## RESULTS AND DISCUSSION

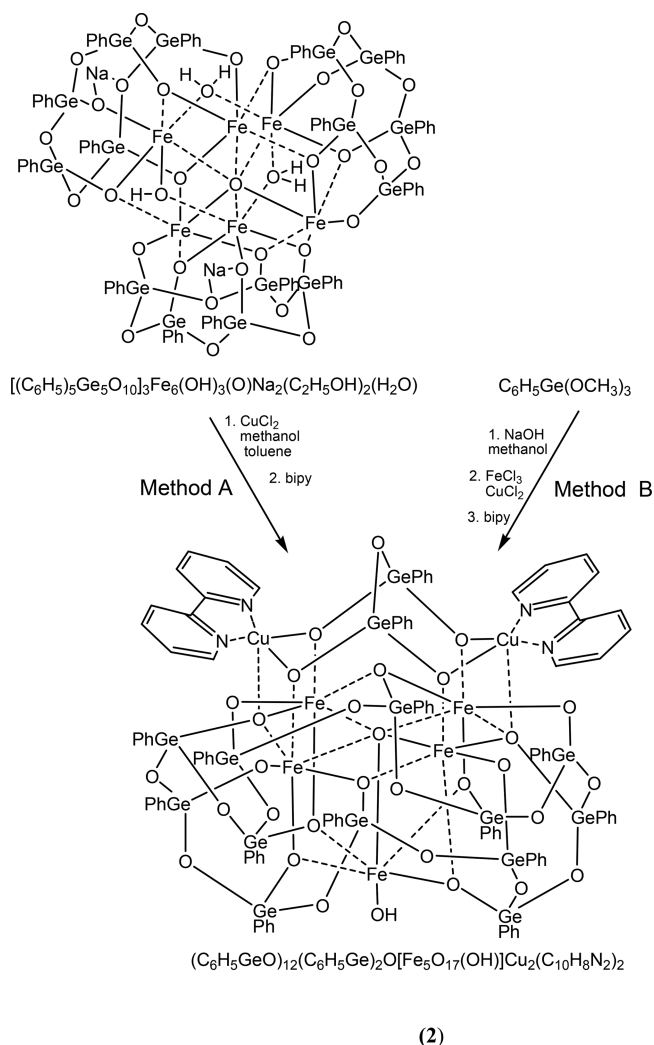
The transmetalation reaction of  $[(\text{Ph}_5\text{Ge}_5\text{O}_{10})_3\text{Fe}_6(\text{OH})_3(\text{O})\text{Na}_2]\cdot 2\text{EtOH}\cdot\text{H}_2\text{O}$  (**1**) with  $\text{CuCl}_2$  was performed so to substitute sodium ions of **1** by copper atoms with the expected formation of the first example of a cage metallagermsesquioxane containing ions of two different transition metals. The crystallization of the product was found to be a difficult task, most likely due to its good solubility and/or the time required for the process of cage assembly. A change in crystallization systems gave no result, while the use of additional N ligation (from 2,2'-bipyridine) allows isolation in a yield of 9% the crystalline product **2**—heptanuclear  $\text{Fe}_5\text{Cu}_2$ -phenylgermsesquioxane with 2,2'-bipyridines coordinating copper centers (Scheme 1, method A).

Compound **2** (Figure 2, top), despite inheriting at first sight the structural features of initial complex **1**, presents deep changes in molecular organization. Indeed, the central core of Lindqvist ion type ( $\text{Fe}_6\text{O}_{19}$ ) in **1** (Figure 2, bottom left) underwent a  $\text{FeO}$  elimination, forming an  $\text{Fe}_5$ -based cage of  $\text{Fe}_5\text{O}_{18}$  composition, with consequent back-filling of the vacant position by the  $(\text{PhGe})_2\text{O}$  group. Such specific “degradation and replacement” allowed two copper(II) ions to occupy left and right bottom coordination sites at this core with simultaneous formation of the earlier unknown mixed oxo cluster of composition  $\text{Cu}_2\text{Fe}_5\text{Ge}_2\text{O}_{19}$  (Figure 2, bottom right).

Quite logically, the shift in metal content/location causes changes in composition/structure of germsesquioxane ligands. In comparison to **1**, containing three ligand of the same type, a cisoid pentameric cycle  $(\text{PhGeO}_{1.5})_5$  (Figure 3, left), the newly synthesized product **2** includes two different germsesquioxane fragments. Namely, these are (i) the digermoxane bridge  $\text{Ph}_2\text{Ge}_2\text{O}_5$ , linking copper(II) ions, and (ii) dodecameric  $[\text{PhGeO}_2]_{12}$  cycle, embracing iron(III) centers (Figure 3, right). This is the first observation of such germsesquioxane ligands for all earlier described types of metallagermsesquioxanes.<sup>3–5</sup>

Our further investigations showed that the yield of this fascinating compound **2** could be increased using a self-assembling reaction (Scheme 1, method B). This synthetic regime allows consideration of the desired atomic ratio for the reaction ( $\text{Ge}_{14}:\text{Cu}_2:\text{Fe}_5:\text{N}_4$ ). These precise loadings of reactants favor the formation of target compound **2** (in case of method A the reactant atomic ratio is limited by a certain composition of compound **1**). Finally, this method leads to the isolation of product **2** in higher yield (21%). For both synthetic routes

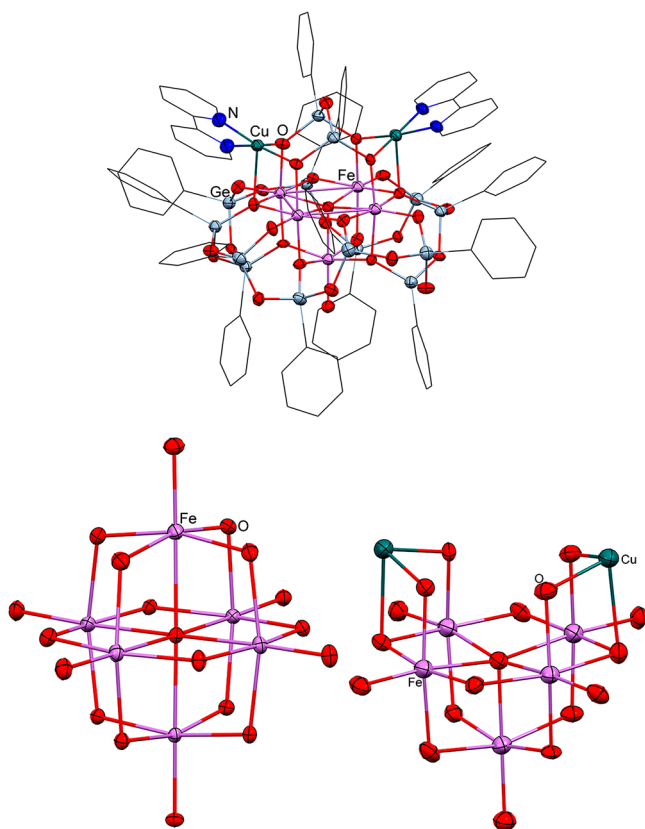
## Scheme 1. Synthetic Pathways to Heptanuclear $\text{Fe}_5\text{Cu}_2$ -Phenylgermsesquioxane with 2,2'-Bipyridines **2**



(methods A and B) an exclusive interaction of bipyridine ligands with copper centers occurs while iron centers prefer to arrange in an  $\text{Fe}_5\text{Ge}_2\text{O}_{19}$  core, indicating its high stability.

We have found that complex **2** is an excellent catalyst in alkane oxidation with hydrogen peroxide at low temperature (40–50 °C). An example of cyclohexane oxidation is shown in Figure 4. The yield of products is negligible if  $\text{HNO}_3$  is not added to the reaction solution. The acid possibly breaks some bonds between germanium atoms and ions of copper and/or iron. This opens the approach of catalytically active species to the substrate.

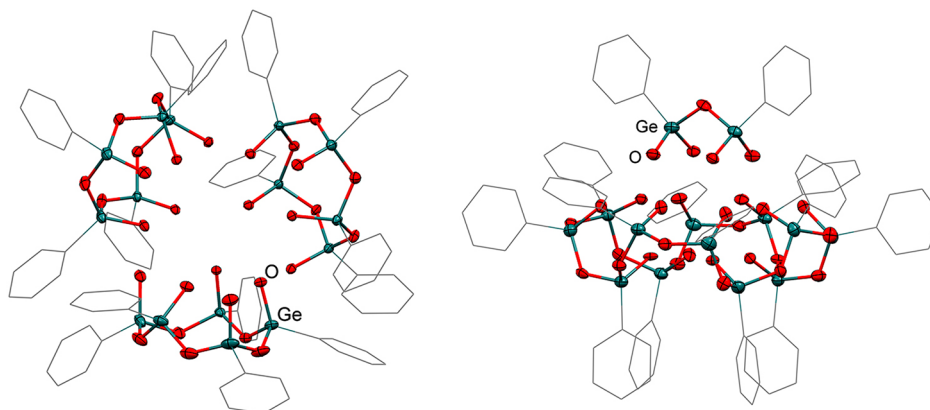
To get an insight into the nature of oxidizing species, we measured the selectivity of C(1), C(2), C(3), and C(4) parameters in oxidations of linear (*n*-heptane) and branched cyclic saturated (methylcyclohexane) hydrocarbons with  $\text{H}_2\text{O}_2$ . The regioselectivity parameters (relative normalized reactivities of hydrogen atoms at carbon atoms C(1), C(2), C(3), and C(4) of the *n*-heptane chain) determined for the oxidation of *n*-heptane are summarized in Table 1. The values of these parameters are close to those determined by us previously for the oxidations by the systems which operate with the formation of hydroxyl radicals.<sup>19</sup> The bond-selectivity parameter (1°:2°:3°; the relative normalized reactivities of hydrogen atoms at the primary, secondary, and tertiary carbons) in the



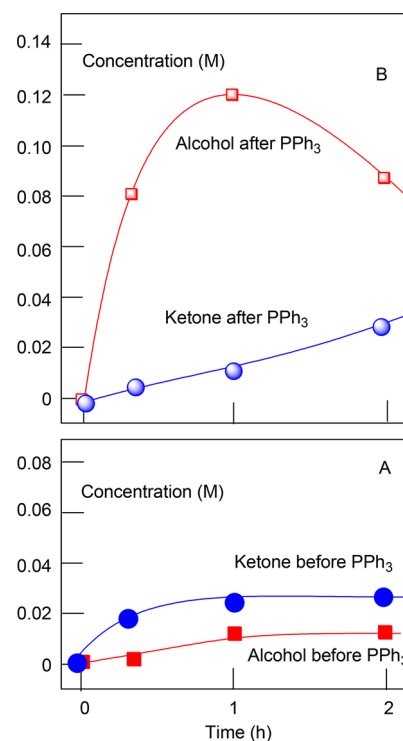
**Figure 2.** (top) Molecular structure of **2**. (bottom) Simplified view of central metal oxo cores in compounds **1** (left) and **2** (right).

oxidation of methylcyclohexane (1.0:5.8:14.3; see Table 2 and Figure 5) is close to the corresponding values found for the systems oxidizing alkanes with hydroxyl radicals (see, for example, ref 19). The oxygenation of methylcyclohexane (MCH) with  $\text{H}_2\text{O}_2$  proceeds mainly at the tertiary carbon atom with formation of 1-methylcyclohexanol after reduction with  $\text{PPh}_3$  (product **P5**). The GC profile of the products obtained in the oxidation catalyzed by **2** is similar to the profiles reported previously for some other systems which oxidize with the participation of hydroxyl radicals. All these data testify that an oxidizing species generated by the system exhibits a low selectivity typical for hydroxyl radicals.

Complex **2** catalyzes efficient oxidation of alcohols with *t*-BuOOH. Thus, 1-phenylethanol is transformed into acetophe-



**Figure 3.** Simplified view of germanium-based ligands of compounds **1** (left) and **2** (right). Color code: Ge, gray; O, red.



**Figure 4.** (A) Accumulation of cyclohexanol and cyclohexanone in the oxidation of cyclohexane (0.46 M) with hydrogen peroxide (2 M; 50%) catalyzed by complex **2** ( $5 \times 10^{-4}$  M) in the presence of  $\text{HNO}_3$  (0.05 M) in acetonitrile at 40 °C before reduction with  $\text{PPh}_3$ . (B) As in (A) after reduction with  $\text{PPh}_3$ . The yield of the product was 28%; TON = 260.

none in a yield of about 100% after 5 h at 50 °C in the presence of 0.05 M  $\text{HNO}_3$ . Cyclohexanol was oxidized to cyclohexanone in 60% yield after 2 h at 50 °C. Hydrogen peroxide oxidizes cyclohexanol and 2-heptanol in 40 and 43% yields, respectively, at 50 °C in the presence of  $\text{HNO}_3$ .

Seeing the good results of complex **2** in the oxidation of alkanes and alcohols, we decided to evaluate it in the oxidative amidation of alcohols (Scheme 2). This reaction was already reported with copper,<sup>20</sup> iron,<sup>21</sup> and zinc salts,<sup>22</sup> and we demonstrated that copper and iron silsesquioxanes as well as iron germanoxane complexes could be used efficiently with catalyst loadings down to 100 ppm of copper and 500 ppm of iron.<sup>5,23</sup> Since complex **2** features both copper and iron,

**Table 1. Oxidation of *n*-Heptane Catalyzed by Complex 2<sup>a</sup>**

entry	time (min)	isomer	concn (M)	C(1):C(2):C(3):C(4)
1	5	ol-1	0.0006	1:5.0:5.0:4.5
		ol-2	0.002	
		ol-3	0.002	
		ol-4	0.0009	
2	10	ol-1	0.0025	1:6.3:6.3:5.6
		ol-2	0.01	
		ol-3	0.01	
		ol-4	0.0045	
3	60	ol-1	0.003	1:6.5:6.7:7.0
		ol-2	0.013	
		ol-3	0.014	
		ol-4	0.007	

<sup>a</sup>Accumulation of isomers of heptanol (isomeric heptanones are formed in low concentrations after reduction of the reaction mixtures with PPh<sub>3</sub>) in the oxidation of *n*-heptane (0.5 M) with hydrogen peroxide (2 M; 50%) catalyzed by complex 2 (5 × 10<sup>-4</sup> M) and nitric acid (0.05 M) in acetonitrile at 50 °C.

it seemed reasonable to estimate its catalytic activity in the oxidative amidation. Several amines, used as ammonium salts, were reacted with benzylic alcohol in the presence of catalytic quantities of 2. Calcium carbonate, with a high purity of 99.995% to avoid any metallic contamination, and TBHP, which acts as a terminal oxidant, were also added to the reaction mixture. After a quick optimization, it was found that a catalyst loading of 0.4 mol % of complex 2 was found to be the lower limit to obtain reasonable results in terms of yield and efficiency. The difference in activity in comparison to copper and iron silsesquioxanes might result from the germsesquioxane network in catalyst 2. Using 2 as catalyst, secondary amide 3 was isolated in an excellent yield of 93%. The use of cyclohexylamine and *n*-butylamine resulted in pure amides 4 and 5 in 84–85% yields. The use of secondary amines was also found to be efficient, and amides 6 and 7 could be isolated in 82% and 71% yields, respectively. Moreover, turnover number (TON) and turnover frequency (TOF) values up to 232 and 9.7 h<sup>-1</sup> could be obtained, respectively, proving the good efficiency of germsesquioxane compound 2.

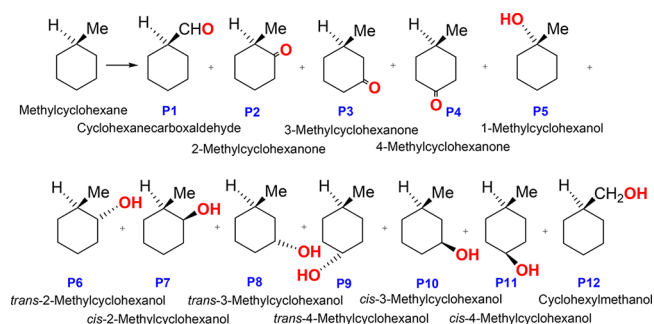
## CONCLUSIONS

A new representative of the rare family of metallagermsesquioxanes has been proved to be available through both self-assembly (from PhGe[OMe]<sub>3</sub>) and transmetalation (of sodium-containing Fe-germsesquioxane) approaches, assisted by the use of 2,2'-bipyridine. These reaction procedures allowed us to isolate the first example of Fe(III)/Cu(II)-phenylgermsesquioxane. Its specific cage-like architecture involves an unusual derivative of a Lindqvist ion (Fe<sub>5</sub>O<sub>18</sub>), which is capable of incorporating copper ions, giving in sum a mixed-metal oxa cluster of

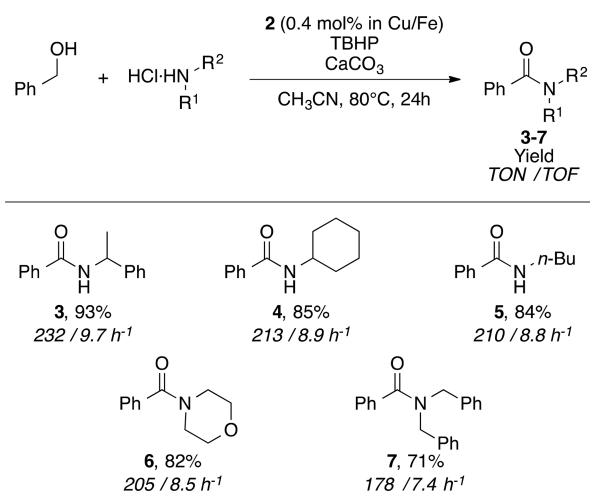
**Table 2. Oxidation of Methylcyclohexane with H<sub>2</sub>O<sub>2</sub> (50% Aqueous) Catalyzed by Complex 2 (5 × 10<sup>-4</sup> M) in the Presence of HNO<sub>3</sub> (0.05 M) in MeCN at 40 °C<sup>a</sup>**

entry	time (min)	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	yield (%)
1	20	0.0	4	4	2	20	11	20	14	7	20	9	4	32
2	60	0.0	9	9	4	20	8	16	12	6	19	9	4	35
3	120	0.4	7	5	2	22	7	14	11	5	16	8	3	24
4	120 <sup>b</sup>	1	12	12	5	9	1	4	4	2	9	5	1	18
5	180	0.0	7	5	2	18	6	11	9	4	13	6	2	23

<sup>a</sup>Concentrations of isomeric ketones and alcohols are given in mM. <sup>b</sup>Concentrations were measured before reduction with PPh<sub>3</sub>.

**Figure 5. Products of the methylcyclohexane oxidation with H<sub>2</sub>O<sub>2</sub> catalyzed by complex 2.**

## Scheme 2. Oxidative Amidation at Low Catalyst Loading<sup>a</sup>



<sup>a</sup>TON = (mmol of product)/(mmol of Cu/Fe). TOF = TON/(reaction time), given in h<sup>-1</sup>.

composition Cu<sub>2</sub>Fe<sub>5</sub>Ge<sub>2</sub>O<sub>19</sub>. This metalla-based fragment is stabilized by O ligation from two types of germanium-based fragments (cyclic Ph<sub>12</sub>Ge<sub>12</sub>O<sub>24</sub> and acyclic Ph<sub>2</sub>Ge<sub>2</sub>O<sub>5</sub>) as well as by N ligation from 2,2'-bipyridines. The presence of three types of metallic centers in 2 (Cu, Fe, Ge) and its good solubility allowed us to observe high catalytic activity in the homogeneous oxidation of alkanes and alcohols as well as in the formation of amides from alcohols. At the moment, it is not possible to conclude if metallagermsesquioxanes are more active precatalysts in comparison to their sister compounds metallasilsesquioxanes due to the presence of metalloidal germanium centers. Despite many examples of Cu-<sup>23a,24</sup> or Fe-based<sup>23b,c</sup> cage silsesquioxanes, tested in catalysis, the pure (Cu/Fe-based) analogue of compound 2 is still unknown in the chemistry of silsesquioxanes. According to the available

information, it could be said that the catalytic activities of metallasilsesquioxanes and metallagermsesquioxanes are comparable.

Synthesis of other mixed-metal germesquioxanes and investigation of their catalytic properties are still intriguing tasks, and corresponding experiments by our team are in progress.

### Accession Codes

CCDC 1572284 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto: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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#### Notes

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