

Article

# Cu<sub>42</sub>Ge<sub>24</sub>Na<sub>4</sub>—A Giant Trimetallic Sesquioxane Cage: Synthesis, Structure, and Catalytic Activity

Alena N. Kulakova <sup>1,2</sup>, Alexey N. Bilyachenko <sup>1,2,\*</sup>, Victor N. Khrustalev <sup>2,3</sup> ,  
Yan V. Zubavichus <sup>3</sup> , Pavel V. Dorovatovskii <sup>3</sup>, Lidia S. Shul'pina <sup>1</sup> , Xavier Bantreil <sup>4</sup>,  
Frédéric Lamaty <sup>4,\*</sup>, Elena S. Shubina <sup>1</sup> , Mikhail M. Levitsky <sup>1</sup> and Georgiy B. Shul'pin <sup>5,6,\*</sup> 

<sup>1</sup> A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova, 28, Moscow 119991, Russia; alenkulakova@gmail.com (A.N.K.); shulpina@ineos.ac.ru (L.S.S.); shu@ineos.ac.ru (E.S.S.); levitsk@ineos.ac.ru (M.M.L.)

<sup>2</sup> People's Friendship University of Russia, ul. Miklukho-Maklaya, dom 6, Moscow 117198, Russia; vnkhrustalev@gmail.com

<sup>3</sup> National Research Center "Kurchatov Institute", pl. Akademika Kurchatova, dom 1, Moscow 123182, Russia; yzubav@googlegmail.com (Y.V.Z.); paulgemini@mail.ru (P.V.D.)

<sup>4</sup> Institut des Biomolécules Max Mousseron (IBMM) UMR 5247, CNRS, Université de Montpellier, ENSCM, Université de Montpellier Campus Triolet Place Eugène Bataillon, 34095 Montpellier CEDEX 5, France; xavier.bantreil@umontpellier.fr

<sup>5</sup> Semenov Institute of Chemical Physics, Russian Academy of Sciences, Ulitsa Kosygina, dom 4, Moscow 119991, Russia

<sup>6</sup> Chair of Chemistry and Physics, Plekhanov Russian University of Economics, Stremyannyi pereulok, dom 36, Moscow 117997, Russia

\* Correspondence: bilyachenko@ineos.ac.ru (A.N.B.); frederic.lamaty@umontpellier.fr (F.L.); gbsh@mail.ru (G.B.S.); Tel.: +7-499-135-9369 (A.N.B.); +33-(0)-4-67-14-38-47 (F.L.); +7-495-939-7317 (G.B.S.)

Received: 18 September 2018; Accepted: 16 October 2018; Published: 22 October 2018



**Abstract:** Unprecedented germanium-based sesquioxane exhibits an extremely high nuclearity (Cu<sub>42</sub>Ge<sub>24</sub>Na<sub>4</sub>) and unusual encapsulation features. The compound demonstrated a high catalytic activity in the oxidative amidation of alcohols, with cost-effective catalyst loading down to 400 ppm of copper, and in the oxidation of cyclohexane and other alkanes with H<sub>2</sub>O<sub>2</sub> in acetonitrile in the presence of nitric acid. Selectivity parameters and the mode of dependence of initial cyclohexane oxidation rate on initial concentration of the hydrocarbon indicate that the reaction occurs with the participation of hydroxyl radicals and alkyl hydroperoxides are formed as the main primary product. Alcohols have been transformed into the corresponding ketones by the catalytic oxidation with *tert*-butyl hydroperoxide.

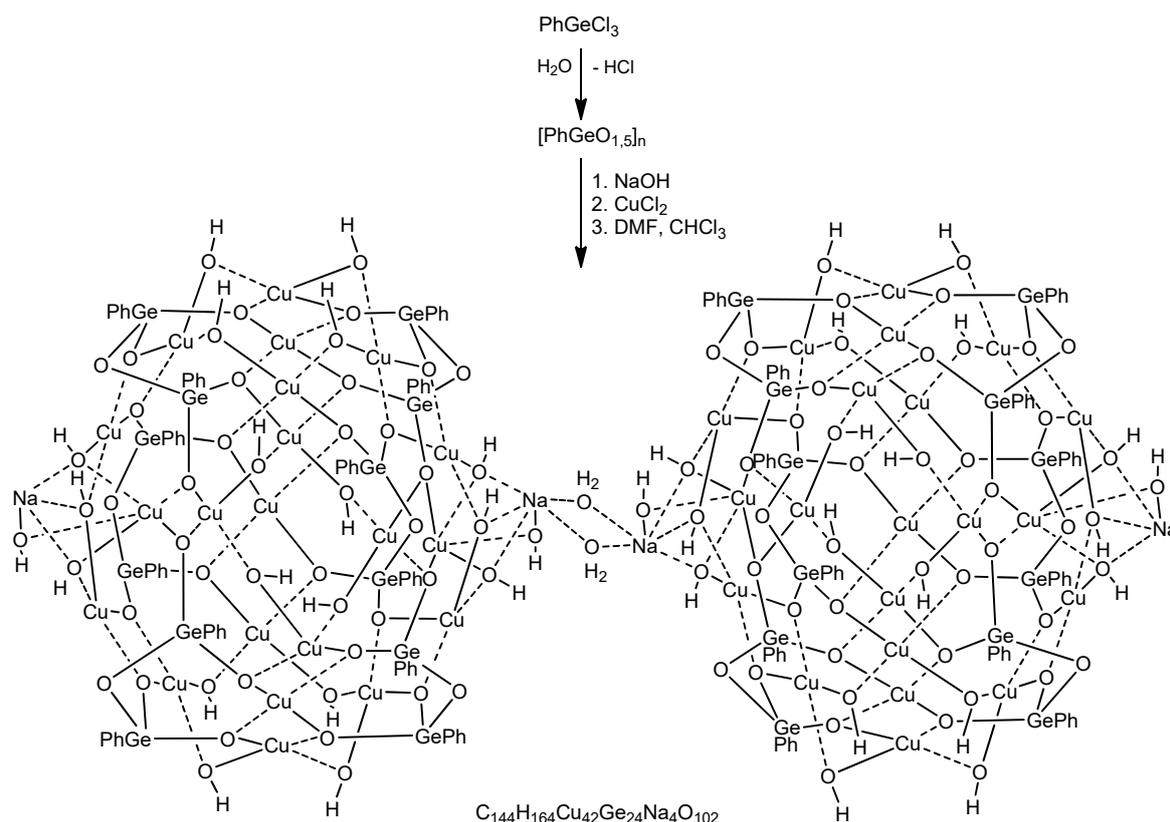
**Keywords:** alkanes; amides; hydrogen peroxide; multinuclear complexes; iron complexes; metallasiloxanes

## 1. Introduction

The interest to cage-like compounds—which find many unique applications [1–4]—is determined by the kaleidoscopic multiplicity of their molecular topologies as well as flexibility in the preparation of either metal-free [5–8] or metal-based [9–12] complexes (with an opportunity to combine several different metal atoms within one molecule). A proper choice of the ligand is of obvious significance for the synthesis of metallacages. For example, heterochained ligands based on (R)Si-O-(R)Si fragments have proven promising for the synthesis of numerous metallacomplexes [4,13–16]. It is the quantity of organic groups at the silicon atoms that are mainly responsible for the resultant complex's molecular topology. Notably, the majority of cage-like metalladerivatives are enabled by branched

monosubstituted ( $\text{RSiO}_{1.5}$ ) silsesquioxane ligands [17–19]. It is ultimately surprising but to the best of our knowledge germanium sesquioxane ligands that are the closest analogues of silsesquioxanes, have been scarcely studied in the context of a possible molecular design of metallacomplexes so far. We could mention here only the use of (i) bis(carboxyethyl)germanium sesquioxide [20–27] in hydrothermal reactions and (ii)  $\text{PhGe}(\text{OMe})_3$  [28,29] in the self-assembly synthesis.

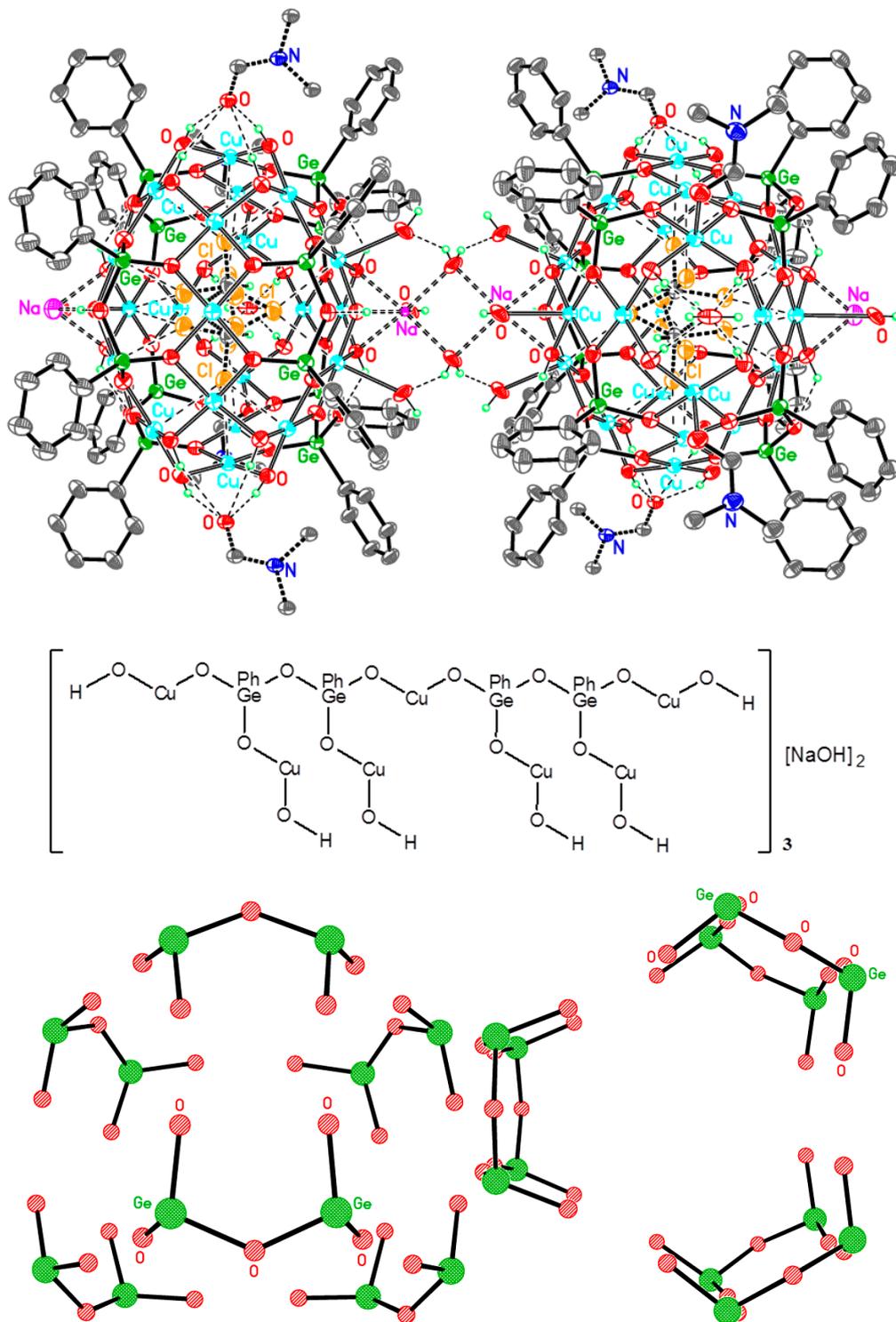
Here we present an alternative convenient and versatile approach to cage-like metallagermaniums sesquioxanes starting from oligomeric  $[\text{PhGeO}_{1.5}]_n$  that is easily accessible via the hydrolytic polycondensation of  $\text{PhGeCl}_3$  (Figure 1). The second step of the synthetic procedure consists in the generation of highly reactive  $\text{PhGeO}^-\text{Na}^+$  fragments through the interaction of  $[\text{PhGeO}_{1.5}]_n$  with sodium hydroxide. It has been revealed that the resulting mixture remained heterogeneous at a 1/1 reactant ratio ( $\text{Na}/\text{Ge} = 1$ ). By increasing this ratio to 3/1 ( $\text{Na}/\text{Ge} = 3$ ), a homogeneous solution is obtained, which is prone to exchange reactions with diverse sources of transition metal ions. A high concentration of sodium centers in the resultant sodium germanolate intermediate (formally, the latter could be regarded as  $\text{PhGe}(\text{ONa})_3$ ) enables the uptake of a significant amount of transition metal ions by a simple and convenient reaction with a transition metal halide. Taking in mind the fact that Cu-based germsesquioxanes remain exclusively rare [24,30], we chose  $\text{CuCl}_2$  as a source of transition metal ions for the very first trial of this reaction (Figure 1). This reaction accomplished in a  $\text{DMF}/\text{CHCl}_3$  solvent system (also used for the crystallization) afforded a totally unexpected title product **1** in a 20% yield.



**Figure 1.** General scheme of synthesis and structure of coppersodiumgermsesquioxane **1**.

The structure of **1**, which is the first observation of a  $\text{Cu}(\text{II}),\text{Na}$ -germsesquioxane cage, is unique both as compared to previously reported Cu-containing germsesquioxanes [24,30] and to the best of our knowledge, to any type of oxametalloclusters. Indeed, the whole complex of **1** is built up of two similar cage units of unprecedented  $\text{Cu}_{21}\text{Ge}_{12}$ -nuclearity. An isolation of such metal-rich (the  $\text{M}/\text{Ge}$  ratio exceeds 1/1) product has never been reported for any metallagermaniums sesquioxanes [20–30]. In terms of topology, the spherical shape of cage-like components of product **1** could be compared

only to non-dimeric Cu(I)-based silsesquioxane reported by the team of Prof. Zhu and Prof. Roesky [31]. An intriguing feature of the spherical cage of **1** is its composition that could be described as a coordination complex of three identical units corresponding to the Cu<sub>7</sub> nuclearity (Figure 2, central panel).



**Figure 2.** Top panel. The molecular structure of **1**. Central panel. A sketch of the cage's building block in **1**. Bottom panel. The structure of acyclic germoxane ligands in **1**.

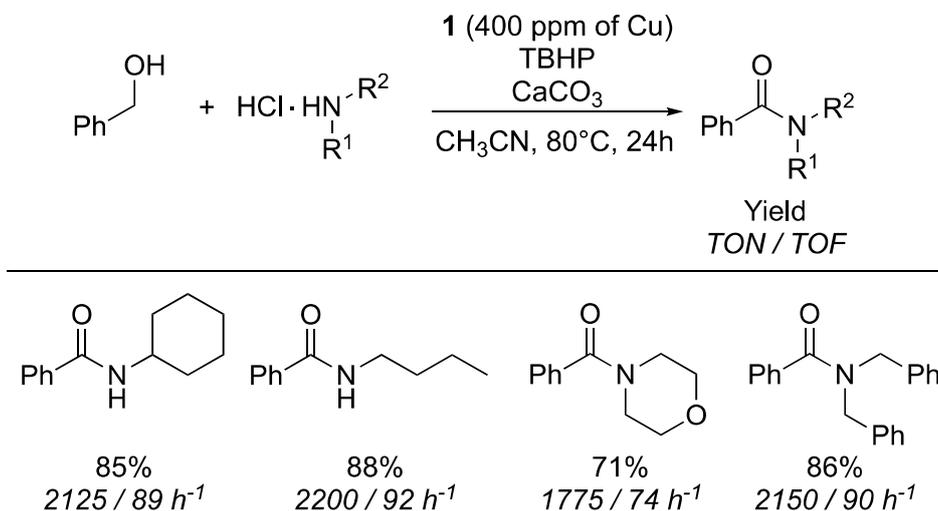
Keeping in mind the extraordinary type of nuclearity manifested by complex **1** a concise survey on related high-nuclearity clusters would be appropriate. A series of 3D open frameworks based on copper-germanium chalcogenides with such building blocks as  $[\text{Cu}_8\text{Ge}_6\text{S}_{18}]^{4-}$ ,  $[\text{Cu}_8\text{Ge}_6\text{Se}_{19}]^{4-}$ ,  $[\text{Cu}_8\text{Ge}_6\text{Se}_{19}]^{6-}$ , and  $[\text{Cu}_{16}\text{Ge}_6\text{Se}_{31}]^{10-}$  have been reported [32,33]. Prof. Fenske and co-authors synthesized and characterized numerous copper-based high-nuclearity selenide and phosphide clusters stabilized by organophosphine ligands [34–36] among which  $\text{Cu}_{146}\text{Se}_{73}(\text{PPh}_3)_{30}$  reported back in 1993 still seems to be record-holding. Germanium is prone to the formation of zeolite-like microporous framework structures built up of structural units  $\text{Ge}_n$  with nuclearities  $n$  ranging from 7 to 10 [37–39]. Among polynuclear clusters retaining intrinsically molecular character, a remarkable series of germanium–tin selenides  $[\text{Ge}_x\text{Sn}_{60-x}\text{Se}_{132}]^{24-}$  is worth noting, which was called by the authors “Zeoball” due to the combination of a spherical shape with zeolite-related composition [40,41].

Despite the high content of copper centers, the dimerization of two cage components in the structure of **1** is realized exclusively through sodium ions located at external positions and coordinated by oxygen centers of (i) four hydroxyl groups and (ii) two bridging water molecules. In turn, copper centers in **1** demonstrate several types of ligation. All copper ions are coordinated by oxa-ligands: (i) hydroxyl groups, (ii) solvating DMF molecule, and (iii) germesquioxane ligands. Noteworthy, all six germanium-containing fragments in compound **1** are bridging acyclic ones corresponding to the  $\text{Ph}_2\text{Ge}_2\text{O}_5$  composition (Figure 2, bottom panel). Thus, **1** becomes the first example of a cage metallagermesquioxane bearing no cyclic germoxane ligands. Second, 21 copper ions in each cage of **1** form three  $\text{Cu}_3\text{O}_8$  and six  $\text{Cu}_2\text{O}_6$  nearly planar fragments, in which the metal atoms are tetra-coordinated in a square-planar fashion. Moreover, six copper atoms are additionally coordinated by two DMF and four OH external ligands, whereas thirteen copper atoms are additionally coordinated by chlorine atoms from the encapsulated chloroform molecule. Only two sterically shielded copper atoms preserve the four-coordinated geometry. The fact of chloroform’s encapsulation by itself is not unusual for the chemistry of cage compounds (more than 10 examples are described in [42]). Nevertheless, no examples of such an encapsulation have been reported so far for metallagermesquioxanes. Furthermore, this feature of product **1** as well as the additional coordination of chlorine atoms to the copper ions point to a possible template effect exerted by  $\text{CHCl}_3$  during the assembly of cage metallagermesquioxanes, which was not emphasized in previous reports [20–30].

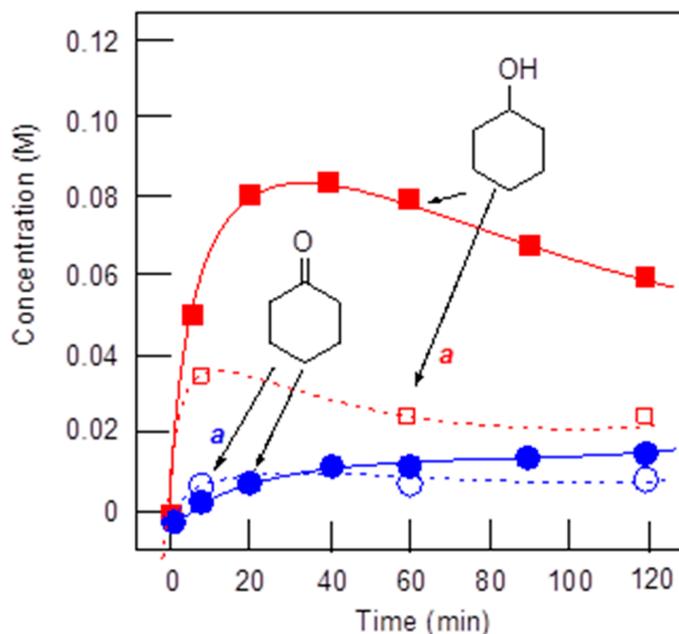
Compound **1** possesses a good solubility in most polar and non-polar aromatic organic solvents. Complex **1** was tested as a catalyst in the homogeneous oxidation. First, **1** was evaluated in the oxidative amidation of benzyl alcohol (Scheme 1). This reaction represents a promising alternative to classical amide bond formation that involves carboxylic acid, amine, and stoichiometric quantities of a coupling agent that could either be toxic or generate stoichiometric quantities of toxic side-products [43]. Herein, benzyl alcohol reacts in the presence of an ammonium chloride, calcium carbonate, *tert*-butyl hydroperoxide (TBHP), and a catalytic quantity of **1**. Corresponding amides could be obtained through a double oxidation of benzyl alcohol into benzaldehyde and then of corresponding hemiaminal into amide. Thanks to the good solubility of **1** in acetonitrile, stock solutions could be prepared and catalyst loading decreased down to 400 ppm of copper for this reaction. Hydrochloride salts of cyclohexyl amine and butyl amine could be converted efficiently with the isolation of corresponding amides in 85% and 88% yields, respectively. Similarly, tertiary amides featuring morpholine and dibenzylamine could be obtained in yields up to 86%. Turnover numbers (TON) and frequencies (TOF) were calculated [44] giving values up to 2200 and  $92 \text{ h}^{-1}$ . This represents a significant improvement compared to our seminal report on copper-catalyzed oxidative amidation (TON = 44, TOF =  $11 \text{ h}^{-1}$ ) [45].

Complex **1** exhibited a high catalytic activity in the oxidation of cyclohexane and other alkanes with  $\text{H}_2\text{O}_2$  in acetonitrile in the presence of nitric acid (Figure 3 and See Supplementary Materials). At lower temperatures, the oxidation is less efficient (See Supplementary Materials). The following selectivity parameters were obtained for the oxidation of *n*-heptane: C(1):C(2):C(3):C(4) = 1.0:7.4:7.2:7.9. These data as well as the character of dependence of the initial cyclohexane oxidation rate on the initial hydrocarbon concentration (approaching a plateau at  $[\text{cyclohexane}]_0 > 0.3 \text{ M}$ ) indicate that

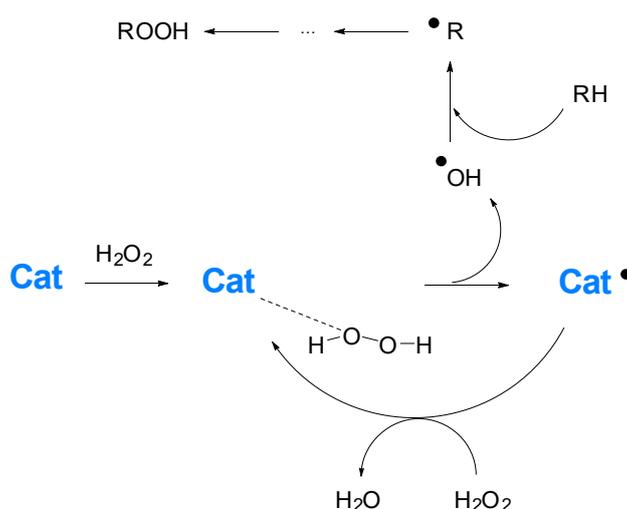
the reaction occurs with the participation of hydroxyl radicals and alkyl hydroperoxides are formed as the main primary products (Figure 4) [46–48]. The oxygenation of *cis*-1,2-dimethylcyclohexane with H<sub>2</sub>O<sub>2</sub> catalyzed by complex **1** gave corresponding isomeric tertiary alcohols in a *trans/cis* ratio of 0.8. The oxidation with *m*-CPBA gave *trans/cis* = 0.5. Alcohols have been efficiently transformed into corresponding ketones by the catalytic oxidation with *tert*-butyl hydroperoxide (See Supplementary Materials).



**Scheme 1.** Catalytic properties of **1** in the oxidative amidation. Reaction conditions: ammonium chloride (0.5 mmol), benzyl alcohol (1.0 mmol), CaCO<sub>3</sub> (0.25 mmol), TBHP (5.5 M, 2.5 mmol), **1** (0.04 mol% of Cu), CH<sub>3</sub>CN (1 mL), 80 °C, 24 h.



**Figure 3.** Accumulation of cyclohexanol and cyclohexanone in the oxidation of cyclohexane (0.46 M) with H<sub>2</sub>O<sub>2</sub> (0.5 M containing 0.94 M H<sub>2</sub>O) catalyzed by complex **1** ( $2.5 \times 10^{-4}$  M) in the presence of HNO<sub>3</sub> (0.05 M) at 40 °C. Concentrations of products were measured by GC after the reduction of the reaction sample with solid PPh<sub>3</sub>. The yield of oxygenates after 60 min was 22% (TON 400). Curves *a*: the same in the absence of HNO<sub>3</sub>.



**Figure 4.** The tentatively proposed catalytic cycle for alkane oxygenation with hydrogen peroxide.

## 2. Conclusions

In conclusion, these studies demonstrate that simple PhGeCl<sub>3</sub> adduct could be converted via “hydrolytic polycondensation—NaOH cleavage—exchange interaction with CuCl<sub>2</sub>” approach into a unique mixed-metal (Cu,Na) germanium-based phenylsesquioxane **1**. This three-stage method allowed to isolate product with an unprecedented high nuclearity (Cu<sub>42</sub>Ge<sub>24</sub>Na<sub>4</sub>) and unusual encapsulation features. Complex **1** exhibited a high catalytic activity in the oxidative amidation of alcohols, with cost-effective catalyst loading down to 400 ppm of copper, and in the oxidation of cyclohexane and other alkanes with H<sub>2</sub>O<sub>2</sub> in acetonitrile in the presence of nitric acid. Selectivity parameters and the mode of dependence of initial cyclohexane oxidation rate on initial concentration of the hydrocarbon indicate that the reaction occurs with the participation of hydroxyl radicals and alkyl hydroperoxides are formed as the main primary product. Alcohols have been transformed into the corresponding ketones by the catalytic oxidation with *tert*-butyl hydroperoxide. The current study advances our basic knowledge of cage metallacomplexes’ self-assembly principles and their application in homogeneous catalysis.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-4344/8/10/484/s1>, Experimental and General procedure for the formation of amides.

**Author Contributions:** A.N.B., F.L., and G.B.S. conceived and designed the experiments; A.N.K., P.V.D., V.N.K., Y.V.Z., X.B., and L.S.S. performed the experiments; A.N.B., F.L., E.S.S., M.M.L., V.N.K., and G.B.S. analyzed the data; E.S.S., and Y.V.Z. contributed reagents/materials/analysis tools; A.N.B., Y.V.Z., F.L., and G.B.S. wrote the paper.

**Acknowledgments:** This work has been supported by the RUDN University Program “5-100”, the Russian Foundation for Basic Research (grant nos. 16-03-00609, 16-03-00254, 16-53-150008, 16-29-05180), the French Embassy in Moscow, and the University of Montpellier, CNRS (Programme de Recherche Conjoint). Synchrotron single-crystal diffraction measurements were performed at the unique scientific facility Kurchatov Synchrotron Radiation Source supported by the Ministry of Education and Science of the Russian Federation (project code RFMEFI61917X0007).

**Conflicts of Interest:** The authors declare no conflict of interest.

## References and Note

1. Fiedler, D.; Leung, D.H.; Bergman, R.G.; Raymond, K.N. Selective molecular recognition, C–H bond activation, and catalysis in nanoscale reaction vessels. *Acc. Chem. Res.* **2005**, *38*, 349–358. [[CrossRef](#)] [[PubMed](#)]
2. Zarra, S.; Wood, D.M.; Roberts, D.A.; Nitschke, J.R. Molecular containers in complex chemical systems. *Chem. Soc. Rev.* **2015**, *44*, 419–432. [[CrossRef](#)] [[PubMed](#)]

3. Cook, T.R.; Stang, P.J. Recent developments in the preparation and chemistry of metallacycles and metallacages via coordination. *Chem. Rev.* **2015**, *115*, 7001–7045. [[CrossRef](#)] [[PubMed](#)]
4. Vardhan, H.; Yusubov, M.; Verpoort, F. Self-assembled metal-organic polyhedra: An overview of various applications. *Coord. Chem. Rev.* **2016**, *306*, 171–194. [[CrossRef](#)]
5. *Carbocyclic Cage Compounds: Chemistry and Applications*; Osawa, E.; Yonemitsu, O. (Eds.) Wiley-VCH: Hoboken, NJ, USA, 1992; p. 409.
6. Tozawa, T.; Jones, J.T.A.; Swamy, S.I.; Jiang, S.; Adams, D.J.; Shakespeare, S.; Clowes, R.; Bradshaw, D.; Hasell, T.; Chong, S.Y.; et al. Porous organic cages. *Nat. Mater.* **2009**, *8*, 973–978. [[CrossRef](#)] [[PubMed](#)]
7. Zhang, G.; Mastalerz, M. Organic cage compounds—From shape-persistency to function. *Chem. Soc. Rev.* **2014**, *43*, 1934–1947. [[CrossRef](#)] [[PubMed](#)]
8. Santolini, V.; Miklitz, M.; Berardo, E.; Jelfs, K.E. Topological landscapes of porous organic cages. *Nanoscale* **2017**, *9*, 5280–5298. [[CrossRef](#)] [[PubMed](#)]
9. Smulders, M.M.J.; Riddell, I.A.; Browne, C.; Nitschke, J.R. Building on architectural principles for three-dimensional metallocupramolecular construction. *Chem. Soc. Rev.* **2013**, *42*, 1728–1754. [[CrossRef](#)] [[PubMed](#)]
10. Ward, M.D.; Raithby, P.R. Functional behaviour from controlled self-assembly: Challenges and prospects. *Chem. Soc. Rev.* **2013**, *42*, 1619–1636. [[CrossRef](#)] [[PubMed](#)]
11. Bloch, W.M.; Clever, G.H. Integrative self-sorting of coordination cages based on ‘naked’ metal ions. *Chem. Commun.* **2017**, *53*, 8506–8516. [[CrossRef](#)] [[PubMed](#)]
12. Zhang, Y.-Y.; Gao, W.-X.; Lin, L.; Jin, G.-X. Recent advances in the construction and applications of heterometallic macrocycles and cages. *Coord. Chem. Rev.* **2017**, *344*, 323–344. [[CrossRef](#)]
13. Murugavel, R.; Voigt, A.; Walawalkar, M.G.; Roesky, H.W. Hetero- and metallasiloxanes derived from silanediols, disilanols, silanetriols, and trisilanols. *Chem. Rev.* **1996**, *96*, 2205–2236. [[CrossRef](#)] [[PubMed](#)]
14. Lorenz, V.; Fischer, A.; Gießmann, S.; Gilje, J.W.; Gun’ko, Y.; Jacob, K.; Edelmann, F.T. Disiloxanediolates and polyhedral metallasilsesquioxanes of the early transition metals and f-elements. *Coord. Chem. Rev.* **2000**, *206–207*, 321–368. [[CrossRef](#)]
15. Pinkert, D.; Limberg, C. Iron silicates, iron-modulated zeolite catalysts, and molecular models thereof. *Chem. Eur. J.* **2014**, *20*, 9166–9175. [[CrossRef](#)] [[PubMed](#)]
16. Levitsky, M.M.; Bilyachenko, A.N. Modern concepts and methods in the chemistry of polyhedral metallasiloxanes. *Coord. Chem. Rev.* **2016**, *306*, 235–269. [[CrossRef](#)]
17. Roesky, H.W.; Anantharaman, G.; Chandrasekhar, V.; Jancik, V.; Singh, S. Control of molecular topology and metal nuclearity in multimetallic assemblies: Designer metallocupramolecular structures derived from silanetriols. *Chem. Eur. J.* **2004**, *10*, 4106–4114. [[CrossRef](#)] [[PubMed](#)]
18. Lorenz, V.; Edelmann, F.T. Metallasilsesquioxanes. *Adv. Organomet. Chem.* **2005**, *53*, 101–153.
19. Edelmann, F.T. Metallasilsesquioxanes. Synthetic and Structural Studies. In *Silicon Chemistry: From the Atom to Extended Systems*; Jutzi, P., Schubert, U., Eds.; Wiley: Hoboken, NJ, USA, 2007; pp. 383–394.
20. He, H.; Cao, G.-J.; Zheng, S.-T.; Yang, G.-Y. Lanthanide germanate cluster organic frameworks constructed from {Ln<sub>8</sub>Ge<sub>12</sub>} or {Ln<sub>11</sub>Ge<sub>12</sub>} cage cluster building blocks. *J. Am. Chem. Soc.* **2009**, *131*, 15588–15589. [[CrossRef](#)] [[PubMed](#)]
21. Cao, G.-J.; Zheng, S.-T.; Zhao, N.; Sun, J.-K.; Yang, G.-Y. Metal–organogermanate frameworks built by two kinds of infinite Ge–O chains with high thermostability and luminescent properties. *Inorg. Chem.* **2010**, *49*, 10211–10213. [[CrossRef](#)] [[PubMed](#)]
22. Stock, N.; Jargstorff, C.; Wriedt, S. Two new crystalline organogermanate-based inorganic-organic hybrid compounds. *Z. Anorg. Allg. Chem.* **2011**, *637*, 572–577. [[CrossRef](#)]
23. Schmidt, C.; Lieb, A.; Stock, N. Synthesis and characterization of the organogermanate-based inorganic-organic hybrid compound Ca<sub>2</sub>[(OOCC<sub>2</sub>H<sub>4</sub>Ge)<sub>2</sub>O<sub>3</sub>]<sub>2</sub>·3H<sub>2</sub>O. *Z. Anorg. Allg. Chem.* **2011**, *637*, 2163–2168. [[CrossRef](#)]
24. Schmidt, C.; Stock, N. High-throughput and in situ energy dispersive X-ray diffraction investigation on the formation of the new metal organogermanate Cu(OOCC<sub>2</sub>H<sub>4</sub>Ge)<sub>2</sub>O<sub>3</sub>. *Cryst. Growth Des.* **2011**, *11*, 5682–5687. [[CrossRef](#)]
25. Li, L.L.; Pan, R.; Zhao, J.W.; Yang, B.F.; Yang, G.Y. A series of lanthanide germanate cluster organic frameworks. *Dalton Trans.* **2016**, *45*, 11958–11967. [[CrossRef](#)] [[PubMed](#)]

26. Li, L.-L.; Cao, G.-J.; Zhao, J.-W.; He, H.; Yang, B.-F.; Yang, G.-Y. Lanthanide germanate cluster organic frameworks based on  $\{Ln_8Ge_{12}\}$  clusters: From one-dimensional chains to two-dimensional layers and three-dimensional frameworks. *Inorg. Chem.* **2016**, *55*, 5671–5683. [[CrossRef](#)] [[PubMed](#)]
27. Liu, X.; Tan, X.-F.; Zhou, J. Hydrothermal syntheses and crystal structure of a new organic hybrid holmium–germanate oxo-cluster. *J. Clust. Sci.* **2017**, *28*, 3209–3215. [[CrossRef](#)]
28. Bilyachenko, A.N.; Levitsky, M.M.; Yalymov, A.I.; Korlyukov, A.A.; Khrustalev, V.N.; Vologzhanina, A.V.; Shul'pina, L.S.; Ikonnikov, N.S.; Trigub, A.L.; Dorovatovskii, P.V.; et al. Cage-like Fe,Na-germsesquioxanes: Structure, magnetism, and catalytic activity. *Angew. Chem. Int. Ed.* **2016**, *55*, 15360–15363. [[CrossRef](#)] [[PubMed](#)]
29. Kulakova, A.N.; Bilyachenko, A.N.; Korlyukov, A.A.; Long, J.; Levitsky, M.M.; Shubina, E.S.; Guari, Y.; Larionova, J. New  $Ni_4Na_2$ -phenylgermsesquioxane architecture: Synthesis, structure and slow dynamic behaviour. *Dalton Trans.* **2018**, *47*, 6893–6897. [[CrossRef](#)] [[PubMed](#)]
30. Bilyachenko, A.N.; Khrustalev, V.N.; Zubavichus, Y.V.; Shul'pina, L.S.; Kulakova, A.N.; Bantreil, X.; Lamaty, F.; Levitsky, M.M.; Gutsul, E.I.; Shubina, E.S.; et al. Heptanuclear  $Fe_5Cu_2$ -phenylgermsesquioxane containing 2,2-bipyridine: Synthesis, structure, and catalytic activity in oxidation of CH compounds. *Inorg. Chem.* **2018**, *57*, 528–534. [[CrossRef](#)] [[PubMed](#)]
31. Tan, G.; Yang, Y.; Chu, C.; Zhu, H.; Roesky, H.W.  $Cu_{24}O_{24}Si_8R_8$ : Organic soluble 56-membered copper(I) siloxane cage and its use in homogeneous catalysis. *J. Am. Chem. Soc.* **2010**, *132*, 12231–12233. [[CrossRef](#)] [[PubMed](#)]
32. Luo, M.; Hu, D.; Yang, H.; Li, D.; Wu, T. PCU-type copper-rich open-framework chalcogenides: Pushing up the length limit of the connection mode and the first mixed-metal  $[Cu_7GeSe_{13}]$  cluster. *Inorg. Chem. Front.* **2017**, *4*, 387–392. [[CrossRef](#)]
33. Wang, Y.-L.; Zhang, B.; Li, W.-A.; Feng, M.-L.; Huang, X.-Y. Two new 3D heterometallic chalcogenides based on copper-rich selenogermanate clusters. *Inorg. Chem. Commun.* **2017**, *85*, 41–44. [[CrossRef](#)]
34. Krautscheid, H.; Fenske, D.; Baum, G.; Semmelmann, M. A new copper selenide cluster with  $PPh_3$  ligands:  $[Cu_{146}Se_{73}(PPh_3)_{30}]$ . *Angew. Chem. Int. Ed.* **1993**, *32*, 1303–1305. [[CrossRef](#)]
35. Fenske, D.  $[Cu_96P_{30}\{P(SiMe_3)_2\}_6(PEt_3)_{18}]$ , a New Phosphorus-Bridged Copper Cluster. *Angew. Chem. Int. Ed.* **1994**, *33*, 1290–1292. [[CrossRef](#)]
36. Zhu, N.; Fenske, D. Novel Cu–Se clusters with Se–layer structures:  $[Cu_{32}Se_7(SenBu)_{18}(PiPr_3)_6]$ ,  $[Cu_{50}Se_{20}(SetBu)_{10}(PiPr_3)_{10}]$ ,  $[Cu_{73}Se_{35}(SePh)_3(PiPr_3)_{21}]$ ,  $[Cu_{140}Se_{70}(PEt_3)_{34}]$  and  $[Cu_{140}Se_{70}(PEt_3)_{36}]$ . *J. Chem. Soc. Dalton Trans.* **1999**, 1067–1076. [[CrossRef](#)]
37. Zhou, Y.; Zhu, H.; Chen, Z.; Chen, M.; Xu, Y.; Zhang, H.; Zhao, D. A large 24-membered-ring germanate zeolite-type open-framework structure with three-dimensional intersecting channels. *Angew. Chem. Int. Ed.* **2001**, *113*, 2224–2226. [[CrossRef](#)]
38. Huang, S.; Christensen, K.; Peskov, M.V.; Yang, S.; Li, K.; Zou, X.; Sun, J. Two open-framework germanates with nickel complexes incorporated into the framework. *Inorg. Chem.* **2011**, *50*, 9921–9923. [[CrossRef](#)] [[PubMed](#)]
39. Inge, A.K.; Sun, J.; Moraga, F.; Guo, B.; Zou, X. Three low-dimensional open-germanates based on the 44 net. *CrystEngComm.* **2012**, *14*, 5465–5471. [[CrossRef](#)]
40. Lin, Y.; Massa, W.; Dehnen, S. “Zeoball”  $[Sn_{36}Ge_{24}Se_{132}]_{24-}$ : A molecular anion with zeolite-related composition and spherical shape. *J. Am. Chem. Soc.* **2012**, *134*, 4497–4500. [[CrossRef](#)] [[PubMed](#)]
41. Santner, S.; Yogendra, S.; Weigand, J.J.; Dehnen, S. Exploring the chemical reaction space at the formation of chalcogenidometalate superspheres in ionic liquids. *Chem. Eur. J.* **2017**, *23*, 1999–2004. [[CrossRef](#)] [[PubMed](#)]
42. Voloshin, Y.; Belaya, I.; Krämer, R. *The Encapsulation Phenomenon. Synthesis, Reactivity and Applications of Caged Ions and Molecules*; Springer: Midtown Manhattan, NY, USA, 2016; p. 638.
43. De Figueiredo, R.M.; Suppo, J.-S.; Campagne, J.-M. Nonclassical routes for amide bond formation. *Chem. Rev.* **2016**, *116*, 12029–12122. [[CrossRef](#)] [[PubMed](#)]
44. See ESI (Section 2.4. Calculation of TON and TOF) for details on TON and TOF.
45. Bantreil, X.; Fleith, C.; Martinez, J.; Lamaty, F. Copper-catalyzed direct synthesis of benzamides from alcohols and amines. *ChemCatChem* **2012**, *4*, 1922–1925. [[CrossRef](#)]
46. Shul'pin, G.B. Alkane-Oxidizing Systems Based on Metal Complexes. Radical versus Non-Radical Mechanisms. In *Alkane Functionalization*; Pombeiro, A.J.L., Ed.; Wiley-VCH: Hoboken, NJ, USA, 2018; Chapter 2; pp. 3–13.

47. Shul'pin, G.B. Selectivity enhancement in functionalization of C–H bonds: A review. *Org. Biomol. Chem.* **2010**, *8*, 4217–4228. [[CrossRef](#)] [[PubMed](#)]
48. Shul'pin, G.B. New trends in oxidative functionalization of carbon–hydrogen bonds: A Review. *Catalysts* **2016**, *6*, 50. [[CrossRef](#)]



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).