



Cage-like Fe_xNa-Germesquioxanes: Structure, Magnetism, and Catalytic Activity

Alexey Bilyachenko, Mikhail Levitsky, Alexey Yalymov, Alexander Korlyukov, Viktor Khrustalev, Anna Vologzhanina, Lidia Shul'Pina, Nikolay Ikonnikov, Alexander Trigub, Pavel Dorovatovskii, et al.

► To cite this version:

Alexey Bilyachenko, Mikhail Levitsky, Alexey Yalymov, Alexander Korlyukov, Viktor Khrustalev, et al.. Cage-like Fe_xNa-Germesquioxanes: Structure, Magnetism, and Catalytic Activity. *Angewandte Chemie*, 2016, 128 (49), pp.15586-15589. 10.1002/ange.201607189 . hal-03079229

HAL Id: hal-03079229

<https://hal.science/hal-03079229>

Submitted on 2 Feb 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Cage-like Fe,Na-Germesquioxanes: Structure, Magnetism, and Catalytic Activity

Alexey N. Bilyachenko,* Mikhail M. Levitsky, Alexey I. Yalymov, Alexander A. Korlyukov, Viktor N. Khrustalev, Anna V. Vologzhanina, Lidia S. Shul'pina, Nikolay S. Ikonnikov, Alexander E. Trigub, Pavel V. Dorovatovskii, Xavier Bantreil, Frédéric Lamaty,* Jérôme Long, Joulia Larionova, Igor E. Golub, Elena S. Shubina, and Georgiy B. Shul'pin*

Abstract: A series of four unprecedented heterometallic metallagermsesquioxanes were synthesized. Their cage-like architectures have a unique type of molecular topology consisting of the hexairon oxo $\{Fe_6O_{10}\}$ core surrounded in a triangular manner by three cyclic germoxanolates $[PhGe(O)O]_5$. This structural organization induces antiferromagnetic interactions between the Fe^{III} ions through the oxygen atoms. Evaluated for this first time in catalysis, these compounds showed a high catalytic activity in the oxidation of alkanes and the oxidative formation of benzamides from alcohols.

The design of metal-based polycyclic cage-like compounds has attracted a great deal of attention from researchers worldwide over several decades owing to their structural diversity and their potential technological applications especially in catalysis.^[1] Numerous metal–oxygen clusters,^[1b,c,j] metal–organic frameworks^[1d,l,m] or metal–organic polyhedrons^[1f,n] have been designed by using a variety of self-assembling or templated reactions. Among those, a wide family of polynuclear cage-like metallasilsesquioxanes (CLMSs) architectures with interesting structural topologies^[2] and important catalytic activity (e.g. in epoxidation, oxidation and polymerization)^[3] has been synthesized through a reaction involving transition-metal ions and

silsesquioxane $[RSiO_{1.5}]_n$ ligands. Surprisingly, examples of cage-like architectures involving another metalloid close to silicon, namely germanium, are scarce despite the great potential of this element in organometallic chemistry. To our knowledge there is only a series of compounds obtained from germasesquioxane $[RGeO_{1.5}]_2$ ($R = HOOCH_2CH_2$) and various cations.^[4] Their hydrothermal synthesis requires relatively hard conditions consisting of several days of reactions at 110 °C. It is worth mentioning that to date focus has only been on the synthesis, thermogravimetric analysis, luminescence, and sorption properties of these architectures and no investigation of the catalytic activity of metallagermanates has been reported.

Herein, we report an alternative and simplified synthetic approach to design a series of unprecedented individual cage-like metallagermsesquioxanes under mild conditions. In addition, the catalytic activity and magnetic properties of the metallagermsesquioxanes will be discussed.

The single crystals of Fe,Na-phenylgermsesquioxane $[(Ph_5Ge_5O_{10})_3Fe_6(OH)_3(O)Na_2]\cdot(EtOH)_2\cdot H_2O$ **1** (10% yield) were obtained by a reaction between phenyltrimethoxygermane $PhGe(OMe)_3$, NaOH and anhydrous $FeCl_3$ in ethanol with further crystallization. The addition of N-containing ligands, such as phenanthroline, bipyridine, or neocuproine to this reaction allowed us to isolate complexes

[*] Dr. A. N. Bilyachenko, Dr. M. M. Levitsky, A. I. Yalymov, Prof. A. A. Korlyukov, Prof. V. N. Khrustalev, Dr. A. V. Vologzhanina, L. S. Shul'pina, Dr. N. S. Ikonnikov, Dr. I. E. Golub, Prof. E. S. Shubina A. N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences Vavilov str., 28, Moscow (Russia) E-mail: bilyachenko@ineos.ac.ru Dr. A. N. Bilyachenko, Prof. V. N. Khrustalev People's Friendship University of Russia Miklukho-Maklay Str., 6, 117198, Moscow (Russia) Prof. A. A. Korlyukov Pirogov Russian National Research Medical University Ostrovitianov str., 1, Moscow (Russia) Dr. A. E. Trigub, P. V. Dorovatovskii National Research Center "Kurchatov Institute" Akademika Kurchatova pl., 1, Moscow (Russia) Dr. J. Long, Prof. J. Larionova Institut Charles Gerhardt de Montpellier (ICGM), UMR5253, Equipe IMNO, Université de Montpellier Site Triolet, Place Eugène Bataillon, 34095 Montpellier cedex 5 (France)

Dr. X. Bantreil, Dr. F. Lamaty Institut des Biomolécules Max Mousseron (IBMM), UMR 5247 CNRS Université Montpellier, ENSCM CNRS, Université de Montpellier, ENSCM should be on the same line Université de Montpellier Campus Triolet, Place Eugène Bataillon, 34095 Montpellier cedex 5 (France) E-mail: frederic.lamaty@umontpellier.fr Prof. G. B. Shul'pin Semenov Institute of Chemical Physics Russian Academy of Sciences Ulitsa Kosygina, dom 4, Moscow 119991 (Russia) E-mail: shulpin@chph.ras.ru Prof. G. B. Shul'pin Plekhanov Russian University of Economics Stremyannyi pereulok, dom 36, Moscow 117997 (Russia)

$[(\text{Ph}_5\text{Ge}_5\text{O}_{10})_3\text{Fe}_6(\text{OH})_3(\text{O})\text{Na}_2(\text{phen})] \cdot (\text{EtOH})_4 \cdot (\text{H}_2\text{O})_{0.5}$ (**2**), $[(\text{Ph}_5\text{Ge}_5\text{O}_{10})_6\text{Fe}_6(\text{OH})_3\text{O}\text{Fe}_6(\text{OH})_2(\text{O})_2\text{Na}_3(\text{bipy})] \cdot (\text{EtOH})_{14.5} \cdot (\text{C}_5\text{H}_5\text{N})_{0.5} \cdot (\text{H}_2\text{O})$ (**3**), and $[(\text{Ph}_5\text{Ge}_5\text{O}_{10})_3\text{Fe}_6(\text{OH})_3(\text{O})\text{Na}_2(\text{neocuproine})] \cdot (\text{EtOH})_2 \cdot (\text{H}_2\text{O})_{1.5}$ (**4**; Scheme S1 in the Supporting Information) in higher yields (up to 26%). Single-crystal X-ray diffraction analyses of **1–4** revealed similar structural organization with the cage-like molecular architecture. The complexes are formed by a central hexairon(III) oxo $\{\text{Fe}_6\text{O}_{19}\}$ core, reminiscent of the “Lindqvist polyanion”, coordinated by three pentameric germoxanolate $[\text{PhGe}(\text{O})\text{O}^-]$ ligands, forming an unprecedented three-pointed star geometry.

In the representative crystal structure of **1**, the octahedral iron ions are located in vertexes of an octahedron (Figure 1). They are connected through the central and peripheral oxygen atoms. $\text{Fe}-\text{O}(\text{Fe})$ distances are in the range of 1.99–2.05 Å, those of $\text{Fe}-\text{O}(\text{Ge})$ and $\text{Fe}-\text{Fe}$ are in the range of 1.87–1.90 Å and 3.16–3.27 Å, respectively. In turn, the values of the $\text{Fe}-\text{O}-\text{Fe}$ angle depend on the position of the oxygen atom. It is close to 90° when the oxygen occupies the central position and significantly exceeds 90° in the other cases ($\angle \text{Fe}-\text{O}1-\text{Fe}$: 88.1–91.7°; $\angle \text{Fe}-\text{O}-\text{Fe}$: 101.9–108.2°). The

Pentameric germoxanolate fragment of **1** adopts a crown configuration (Figure S1), with the main structural parameters: $\text{Ge}-\text{O}(\text{Ge})$ 1.740–1.791 Å, $\angle \text{Ge}-\text{O}-\text{Ge}$ 117.6–129.0°. Note that the only example of cyclic germanoxane fragments in metallagermsesquioxane structures describe hexameric units.^[4a] The structural organization of the related compounds **2–4** is similar to **1**. The difference consists in additional coordination of the respective bidentate ligands (1,10-phenanthroline, 2,2'-bipyridine, neocuproine) to the Na ions (Figure S2). Noteworthy is that sodium ions are located in external positions to the cage and, thus, are responsible for the supramolecular packing (Figure S3). According to the higher yields of **2–4** in comparison to **1**, bidentate ligands might give additional stabilization of the metallagermsesquioxane cage and facilitate its crystallization. These results show that germsesquioxanes indeed provide great potential for creation of cage metalladerivatives, even when using simple alkoxygermane as an initial reagent. Drawing an analogy between Fe-based sesquioxanes of germanium and silicon, we would like to emphasize that known types of cage ironsilsesquioxanes (Refs. [2a,c,j]) have quite different structural features in comparison to germanium-based compounds **1–4**. This suggests a unique role of germanium centers in cage-compound formation. Results of EXAFS study on iron and germanium K-edges for **1–4** confirmed that the oxidation states of iron and germanium are +3 and +4, respectively (Figures S4–S5, Tables S3–S4).

The magnetic properties of these compounds, investigated by using a SQUID magnetometer working in the temperature range 1.8–300 K up to 7 T, indicate that they are paramagnetic behavior in this temperature range. The temperature dependence of the magnetic susceptibility for **1** is given as an example (Figure S7, ESI). The room temperature value of χT , equal to $14.29 \text{ cm}^3 \text{ K mol}^{-1}$, is considerably lower than the theoretical one of $26.25 \text{ cm}^3 \text{ K mol}^{-1}$, expected for six non-interacting Fe^{III} ions ($S=5/2$ and $g=2.00$). Such a discrepancy most likely originates from the occurrence of strong antiferromagnetic interactions between the spin carriers that are still operative at room temperature. This is indeed confirmed by the temperature dependence of χT , which reveals a progressive decrease upon cooling to reach $3.80 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K. Antiferromagnetic interactions between the Fe^{III} ions can be mediated through both the central and bridging oxygen atoms, as found in similar hexanuclear architectures.^[5] For temperatures lower than 10 K, a steep decrease of χT occurs and can be assigned to the zero-field splitting and/or intermolecular interactions between the polynuclear complexes. In addition, the non-null value of χT at low temperature indicates the presence of a non-diamagnetic ground state that should be expected for a pure $S=0$ species. This could reflect either the presence of thermally populated excited states or antagonist magnetic interactions mediated by the different bridging oxygen atoms. The field dependence of the magnetization at 1.8 K for **1** further confirms the non-diamagnetic state with a magnetization value of $2.72 \mu_B$ without any evidence of the saturation indicating the presence of a magnetic anisotropy (Figure S8). Alternating current (AC) measurements performed as the temperature dependence of the in-phase (χ') and out-of-phase (χ'') susceptibilities

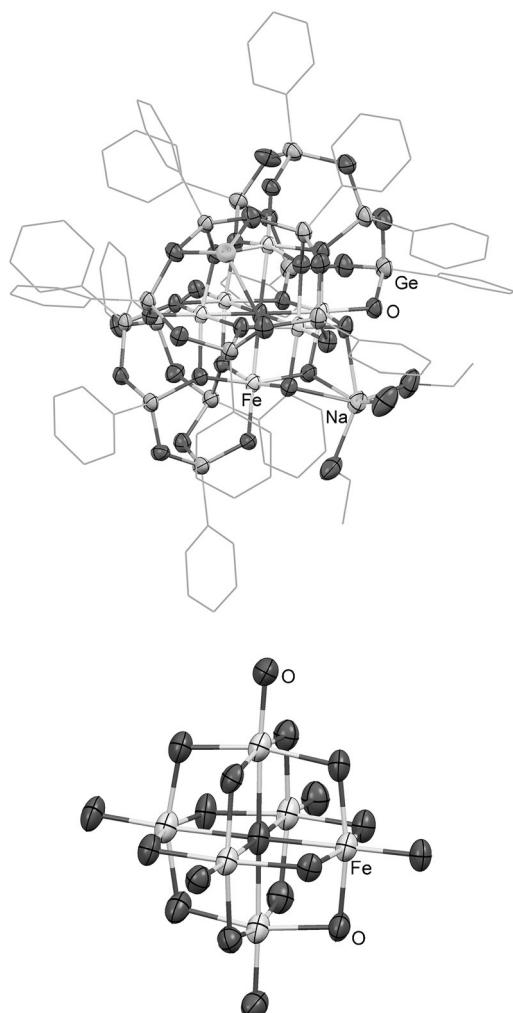


Figure 1. Top: Molecular structure of **1**. Bottom: The structure of Fe_6O_{19} core of **1**. Full color version is given in ESI (Figures S1,S2).

measured in a zero DC magnetic field show an increase upon cooling but without the presence of a maximum, precluding an in-depth characterization of the relaxation dynamics (Figure S9).

We also present herein the first applications of cage metallagermsesquioxanes in catalysis. As complexes **1–4** have similar molecular architectures, we concentrated on the study of one of them as an example, namely, compound **2**. It is well established that iron-based compounds^[6] are capable of catalyzing the oxidation of hydrocarbons with peroxides. We have found that cyclohexane and other alkanes as well as benzene can be oxidized to the alkyl hydroperoxides and phenol, respectively, by hydrogen peroxide in the presence of catalytic amounts of **2** and CF₃COOH (some examples are shown in Figure 2, the experimental details are described in

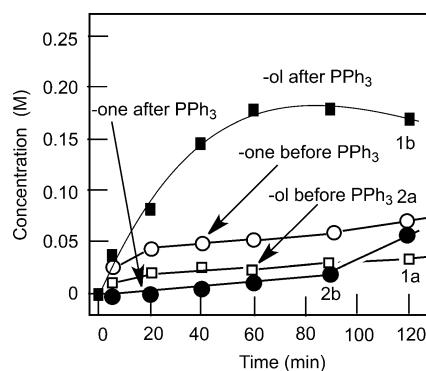


Figure 2. Accumulation of oxygenates (cyclohexanol, curves 1, and cyclohexanone, curves 2) in the oxidation of cyclohexane (0.46 M) with H₂O₂ (50%, aqueous, 1.5 M) catalyzed by **2** (5×10^{-4} M) in the presence of CF₃COOH (0.05 M). Solvent was acetonitrile (total volume of the reaction solution was 5 mL) at 40°C. Concentrations of cyclohexanone and cyclohexanol were determined before (curves a) and after (curves b) reduction of the aliquots with solid PPh₃ (for this method, see Ref. [7]).

the Supporting Information). The oxidation with H₂O₂ catalyzed by complex **2** was very efficient as it gave oxygenates from alkanes in a very high yield of 44 %. This yield is one of the highest values obtained so far in metal-catalyzed oxidations of cyclohexane with H₂O₂ since usually yields are not higher than 5–30 %. For example, cyclohexane oxidation^[6c] with H₂O₂ catalyzed by a hexanuclear iron(III) carboxylate gave maximum yield of oxygenates of 29 %.

The S-shape mode of the initial rate W_0 dependence on the concentration of **2** attests that the reaction order with respect to **2** is not constant and gradually changes from an apparent second order to first order, when $[2]_0$ changes in the interval from 1.5×10^{-4} to 3×10^{-4} M (Figure 3).

On the basis of these data, a mechanism can be proposed which includes a stage of the starting complex monomerization.^[2c] Further dimerization of these particles affords species which are responsible for the catalytic activity of the system.

Dependence of the initial oxidation rate on the concentration of the CF₃COOH co-catalyst is given in Figure S10. The dependence of W_0 on the initial concentration of cyclohexane approaches a plateau at $[CyH]_0 > 0.4$ M (Fig-

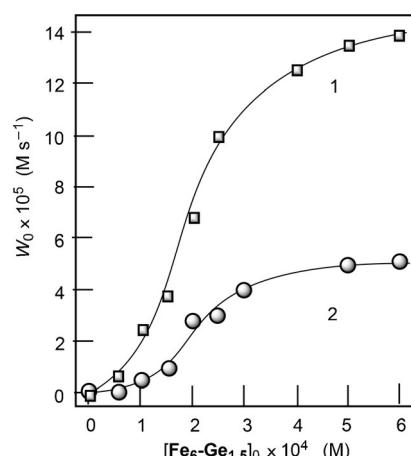


Figure 3. Dependence of the initial rate of oxygenate (the sum cyclohexanol + cyclohexanone) formation W_0 on the initial concentration of **2** in the oxidation of cyclohexane (0.46 M, curve 1) and benzene (0.45 M, curve 2) with hydrogen peroxide (50% aqueous) in the presence of CF₃COOH (0.05 M) in MeCN at 40°C. Concentrations of cyclohexanone and cyclohexanol were determined after reduction of the aliquots with solid PPh₃.

ure S11) indicating a competitive interaction of the oxidizing species with the alkane and acetonitrile.^[8] The rate dependence on the initial concentration of hydrogen peroxide is linear at $[H_2O_2] < 1.5$ M (Figure S12).

Complex **2** was also evaluated in the formation of amides directly from alcohols and amines, in the presence of *tert*-butyl hydroperoxide as the terminal oxidant. For this purpose, we chose the newly developed metal-catalyzed microwave-activated amidation^[9,2c] between benzylic alcohol and (±)-α-methylbenzylammonium chloride (Scheme 1). The use of



Scheme 1. Microwave activation by **2** or FeCl₂·4 H₂O.

complex **2** allowed amide **5** to be obtained in a yield of 71 %. This result was compared to that obtained with a more simple iron salt, FeCl₂·4 H₂O, which gave the product in a yield of only 51 %. This result clearly shows that the germsesquioxane structure exerts a stabilizing effect around the metallic center, resulting in an improved catalytic activity.

In conclusion, a family of unprecedented cage-like Fe₆germsesquioxanes having a central hexairon(III) oxo {Fe₆O₁₀} core coordinated by three pentameric germaxanolate ligands has been obtained. Their structural arrangement induces antiferromagnetic interactions between Fe^{III} ions through the oxygen bridges resulting in a paramagnetic behavior. This class of compounds was evaluated for the first time for its catalytic activity. Complex **2**, displayed a high efficiency in catalysis for alkane oxidation and amide formation from benzylic alcohol and amine. A further investigation on the

design of new metallagermsesquioxanes with different structural organization and catalytic properties is currently in progress. These results, concerning an influence of composition and structure of such cage complexes on catalytic behavior (including possible synergistic effect of metal and germanium ions as catalytic centers) will be presented in the near future.

Acknowledgements

This work was supported by RFBR (projects 16-03-00609, 16-03-00206, 16-03-00254, 16-29-05180, 16-53-150008). French Embassy in Moscow, Balard Foundation, University of Montpellier, CNRS (Programme de Recherche Conjoint), and the Plateforme D'Analyse et de Caractérisation (PAC Balard), and "Science without Borders Program, Brazil-Russia", CAPES (grant A017-2013).

Keywords: cage compounds · homogeneous catalysis · metallagermsesquioxanes · oxidation · structure elucidation

-
- [1] a) M. Veith, *Chem. Rev.* **1990**, *90*, 3–16; b) M. T. Pope, A. Muller, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34–48; *Angew. Chem.* **1991**, *103*, 56–70; c) Special issue on polyoxometalates (Ed.: C. L. Hill), *Chem. Rev.* **1998**, *98*, 1; d) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705–714; e) R. Murugavel, A. Choudhury, M. G. Walawalkar, R. Pothiraja, C. N. R. Rao, *Chem. Rev.* **2008**, *108*, 3549–3655; f) D. J. Tranchemontagne, Z. Ni, M. O'Keeffe, O. M. Yaghi, *Angew. Chem. Int. Ed.* **2008**, *47*, 5136–5147; *Angew. Chem.* **2008**, *120*, 5214–5225; g) T. S. Koblenz, J. Wassenaar, J. N. H. Reek, *Chem. Soc. Rev.* **2008**, *37*, 247–262; h) S. J. Dalgarno, N. P. Power, J. L. Atwood, *Coord. Chem. Rev.* **2008**, *252*, 825–841; i) R. Chakrabarty, P. S. Mukherjee, P. J. Stang, *Chem. Rev.* **2011**, *111*, 6810–6918; j) H. N. Miras, J. Yan, D.-L. Long, L. Cronin, *Chem. Soc. Rev.* **2012**, *41*, 7403–7430; k) M. M. J. Smulders, I. A. Riddell, C. Browne, J. R. Nitschke, *Chem. Soc. Rev.* **2013**, *42*, 1728–1754; l) H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* **2013**, *341*, 1230444; m) S. Chaemchuen, N. A. Kabir, K. Zhou, F. Verpoort, *Chem. Soc. Rev.* **2013**, *42*, 9304–9332; n) N. Ahmad, A. H. Chughtai, H. A. Younus, F. Verpoort, *Coord. Chem. Rev.* **2014**, *280*, 1–27.
- [2] a) M. M. Levitsky, A. N. Bilyachenko, *Coord. Chem. Rev.* **2016**, *306*, 235–269; b) E. V. Beletskiy, Z. Shen, M. V. Riofski, X. Hou, J. R. Gallagher, J. T. Miller, Y. Wu, H. H. Kung, M. C. Kung, *Chem. Commun.* **2014**, *50*, 15699; c) A. N. Bilyachenko, M. M. Levitsky, A. I. Yalymov, A. Korlyukov, A. Vologzhanina, Yu. Kozlov, L. Shul'pina, D. Nesterov, A. Pombeiro, F. Lamaty, X. Bantreil, A. Fetre, D. Liu, J. Martinez, J. Long, J. Larionova, Y. Guari, A. Trigub, Y. Zubavichus, I. E. Golub, O. A. Filippov, E. S.

Shubina, G. B. Shul'pin, *RSC Adv.* **2016**, *6*, 48165–48180; d) A. N. Bilyachenko, A. I. Yalymov, L. S. Shul'pina, D. Mandelli, A. A. Korlyukov, A. V. Vologzhanina, M. A. Es'kova, E. S. Shubina, M. M. Levitsky, G. B. Shul'pin, *Molecules* **2016**, *21*, 665; e) E. V. Beletskiy, Y. Wu, M. C. Kung, H. H. Kung, *Organometallics* **2016**, *35*, 301–302; f) M. S. Raj Prabhu, U. Ugandhara, V. Baskar, *Dalton Trans.* **2016**, *45*, 6963–6967; g) A. N. Bilyachenko, A. I. Yalymov, A. Korlyukov, J. Long, J. Larionova, Y. Guari, A. V. Vologzhanina, M. Eskova, E. S. Shubina, M. M. Levitsky, *Dalton Trans.* **2016**, *45*, 7320–7327; h) A. N. Bilyachenko, A. I. Yalymov, M. M. Levitsky, A. Korlyukov, M. Eskova, J. Long, J. Larionova, Y. Guari, L. S. Shul'pina, N. S. Ikonnikov, A. Trigub, Y. V. Zubavichus, I. E. Golub, E. S. Shubina, G. B. Shul'pin, *Dalton Trans.* **2016**, *45*, 13663–13666; i) K. S. Lokare, N. Frank, B. Brauna-Cula, I. Goikoetxea, J. Sauer, C. Limberg, *Angew. Chem. Int. Ed.* **2016**, *55*, 12325–12329; *Angew. Chem.* **2016**, *128*, 12513–12517; j) A. N. Bilyachenko, A. I. Yalymov, M. M. Levitsky, A. A. Korlyukov, V. N. Khrustalev, L. S. Shul'pina, P. V. Dorovatovskii, M. A. Es'kova, F. Lamaty, X. Bantreil, B. Villemejeanne, J. Martinez, Y. N. Kozlov, N. V. Vorontsov, E. S. Shubina, G. B. Shul'pin, unpublished results.

- [3] a) E. A. Quadrelli, J.-M. Basset, *Coord. Chem. Rev.* **2010**, *254*, 707–728; b) A. J. Ward, A. F. Masters, T. Maschmeyer, *Adv. Silicon Sci.* **2011**, *3*, 135–166; c) M. M. Levitsky, A. I. Yalymov, A. N. Kulakova, A. A. Petrov, A. N. Bilyachenko, *J. Mol. Catal. A* **2016**, DOI: 10.1016/j.molcata.2016.06.016.
- [4] a) H. He, G.-J. Cao, S.-T. Zheng, G.-Y. Yang, *J. Am. Chem. Soc.* **2009**, *131*, 15588–15589; b) G.-J. Cao, S.-T. Zheng, N. Zhao, J.-K. Sun, G.-Y. Yang, *Inorg. Chem.* **2010**, *49*, 10211–10213; c) N. Stock, C. Jargstorff, S. Wriedt, *Z. Anorg. Allg. Chem.* **2011**, *637*, 572–577; d) C. Schmidt, A. Lieb, N. Stock, *Z. Anorg. Allg. Chem.* **2011**, *637*, 2163–2168; e) C. Schmidt, N. Stock, *Cryst. Growth Des.* **2011**, *11*, 5682–5687; f) G.-J. Cao, Q.-L. Li, C. Rong, *Chinese J. Struct. Chem.* **2013**, *32*, 1250–1256.
- [5] A. Cornia, D. Gatteschi, K. Hegetschweiler, L. Hausherr-Primo, V. Gramlich, *Inorg. Chem.* **1996**, *35*, 4414–4419.
- [6] a) *Iron Catalysis in Organic Chemistry* (Ed.: B. Plietker), Wiley-VCH, Weinheim, **2008**; b) K. Schröder, K. Junge, B. Bitterlich, M. Beller, *Top. Organomet. Chem.* **2011**, *33*, 83–109; c) G. Trettenhahn, M. Nagl, N. Neuwirth, V. B. Arion, W. Jary, P. Pöchlauer, W. Schmid, *Angew. Chem. Int. Ed.* **2006**, *45*, 2794–2798; *Angew. Chem.* **2006**, *118*, 2860–2865.
- [7] a) G. B. Shul'pin, *J. Mol. Catal. A* **2002**, *189*, 39–66; b) G. B. Shul'pin, *Catalysts* **2016**, *6*, paper no. 50.
- [8] a) D. S. Nesterov, E. N. Chygorin, V. N. Kokozay, V. V. Bon, R. Boča, Y. N. Kozlov, L. S. Shul'pina, J. Jezierska, A. Ozarowski, A. J. L. Pombeiro, G. B. Shul'pin, *Inorg. Chem.* **2012**, *51*, 9110–9122; b) G. B. Shul'pin, Y. N. Kozlov, L. S. Shul'pina, W. Carvalho, D. Mandelli, *RSC Adv.* **2013**, *3*, 15065–15074; c) M. M. Vinogradov, L. S. Shul'pina, Y. N. Kozlov, A. R. Kudinov, N. S. Ikonnikov, G. B. Shul'pin, *J. Organomet. Chem.* **2015**, *784*, 52–61.
- [9] X. Bantreil, P. Navals, J. Martinez, F. Lamaty, *Eur. J. Org. Chem.* **2015**, *417*–422.