Full Articles

Si—C bond strength in cage-like methylsilsesquioxanes and methyl-bearing metalosilsesquioxanes estimated from DFT calculations

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The strength of the Si—C bond in cage-like methylsilsesquioxanes and methyl-bearing coppersilsesquioxanes was estimated from the Mulliken bond populations calculated using the B3LYP density functional method. The estimation was performed using a linear relation between Mulliken bond populations and the calculated Si—C bond strengths in a series of silanes, which is in good agreement with the published data. The introduction of Cu atoms into the silsesquioxane cage leads to a decrease in the Si—C bond strength, which can be a reason for a considerable decrease in the thermal stability of metalorganosilsesquioxanes compared to their siloxane analogs.

Key words: organosilsesquioxanes, metalorganosilsesquioxanes, density functional theory, B3LYP method, Mulliken bond population, bond strength, thermal stability.

The chemistry of metalorganosiloxanes (MOS) is intensively developed since the 1950s.[1] The introduction of metal atoms into the siloxane cage imparts a number of specific properties to the MOS as compared with their siloxane analogs. This is a reason for increased interest in theoretical and applied studies of low-molecular and polymeric MOS.[2—4] An important achievement in this branch of chemistry of organosilicon compounds is the development of methods for the synthesis of so-called cage-like MOS which contain atoms of transition (M = Cu, Mn, Co, *etc.*) and alkali metals (M′ = Na, K, Li). Cage-like MOS molecules are built of silsesquioxane rings $(RSiO_{1.5})_n$ linked by inter-ring or intra-ring Si—O—M bonds. Among the cage-like MOS, sandwich and globular (or saddle-shape) compounds are mostly known.[5—7] The former contain two silsesquioxane rings and have the general formula $(RSiO_{1.5})_6(MO)_6(RSiO_{1.5})_6$ or $[(RSiO_{1.5})_6](MO)_4(M'O_{0.5})_4(RSiO_{1.5})_6$, whereas the latter have only one ring and the general formula $(RSiO_{1.5})_{12}(MO)_4(M'O_{0.5})_4$. The molecules of cage-like MOS have a regular spatial structure and can crystallize. This permits exact determination of structural parameters and the obtaining of more reliable information on the electronic structure, what can be useful for the under-

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standing of specific features of the behavior of MOS, in particular, the fact that MOS are prone to intra- and intermolecular rearrangements resulting in changes in the molecular configuration[8] and to disproportionation with the formation of new M—O—M and Si—O—Si bonds.[9–11] A substantial decrease in the thermal stability of MOS compared to the siloxane analogs (by ~150 °C for the compounds with phenyl group attached to a silicon atom and even by about 300 °C for those with methyl group attached to Si atom).[7,12] In this connection, elucidation of the effect of the metal atoms introduced into the siloxane skeleton of MOS molecules on the Si—C bond strength is of interest. The aim of the present work is to analyze, in the framework of density functional theory, the electronic structure and energy characteristics of the methyl dervatives of cage-like MOS containing Cu atoms (with emphasis placed on the estimation of the Si—C bond strength) and compare them with those of cage methylsilsesquioxanes.

Calculation Procedure

Quantum chemical calculations of cage-like MOS and silsesquioxane molecules were performed in the framework of the density functional theory within the B3LYP Becke—Lee—Yang—Parr functional[14–16] with the DZ basis set[17] with the use of the GAUSSIAN-98 program package.[13] Calculations of the Si—C bond strengths in molecules **1—5** were based on an approach, according to which the density matrices obtained as a results of quantum chemical calculations can be considered as the source of information on the strengths of particular bonds in the compounds. The Mulliken population of a bond A—B (P_{AB}) is given by[18]

$$P_{AB} = 2 \sum_{i=1} \sum_{\mu \in A} \sum_{\mu \in B} C_{i\nu} C_{i\mu} S_{\mu\nu},$$

where the first summation is performed over all occupied MO, while the second and third summations are performed over the orbitals of the atoms A and B, respectively. The bond population P_{AB} correllates with the bond strength.

Results and Discussion

In the present work, we considered the molecule of $[(CH_3SiO_{1.5})_6]_2(CuO)_6$ (**1**) with a sandwich configuration of siloxane bonds and the sandwich (**2**) and globular (**3**) configurations of the molecule $[(CH_3SiO_{1.5})_6]_2(CuO)_4$-$(NaO_{0.5})_4$ (Fig. 1). The siloxane analogs chosen for comparison were octamethylsilsesquioxane (**4**) and dodecamethylsilsesquioxane (**5**) having cage-like molecules (Fig. 2).

Calculations were carried out using the geometric parameters of the cage-like silsesquioxane molecules

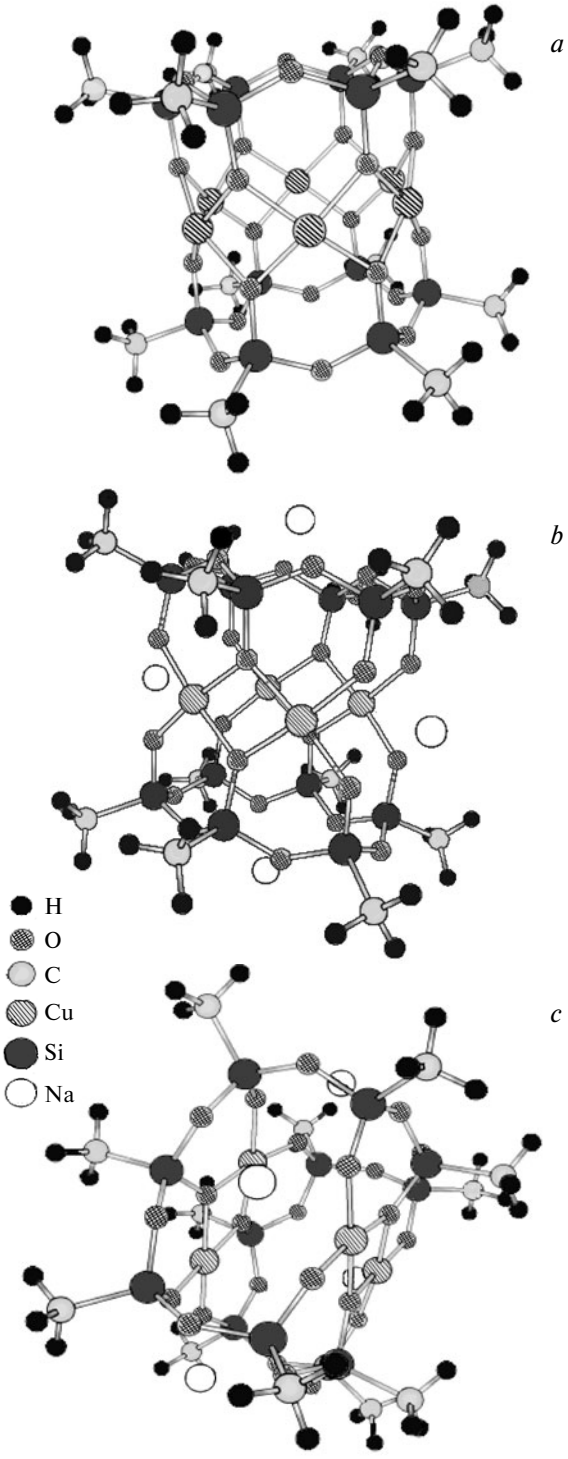

Fig. 1. Structures of crystal solvates of methyl derivatives of metalorganosiloxanes **1** (*a*), **2** (*b*), and **3** (*c*) determined by X-ray analysis. The plots were made using the ChemCraft software.

obtained by X-ray analysis. The structure of compound **4** is available in the literature,[19–20] as well as that of dodecaphenylsilsesquioxane $(C_6H_5SiO_{1.5})_{12}$ with the D_{2d}-silsesquioxane skeleton rather than the D_{6h}-skeleton

Table 1. The total energies (E_{tot}) and the average effective atomic charges (q) in compounds **1—5** calculated by the B3LYP method

Compound	Molecular formula	$-E_{tot}$/au	q_{Si}	$-q_O$*	$-q_C$	q_{Cu}	q_{Na}
1	$Cu_6Si_{12}O_{24}C_{12}H_{36}$	3509.5490	1.763	0.946	1.020	0.827	—
2	$Cu_4Na_4Si_{12}O_{24}C_{12}H_{36}$	3118.2756	1.733	0.979	1.058	0.735	0.865
3	$Cu_4Na_4Si_{12}O_{24}C_{12}H_{36}$	3118.4094	1.716	0.972	1.037	0.820	0.800
4	$Si_8O_{12}C_8H_{24}$	1254.1182	1.836	1.026	1.009	—	—
5	$Si_{12}O_{18}C_{12}H_{36}$	1881.1751	1.882	1.043	1.035	—	—

* The average atomic charge on the siloxane ring oxygens and on the out-of-siloxane ring oxygens.

in the cage-like MOS molecules with the sandwich configuration.[21,22] Since even DFT calculations with the relatively simple valence basis set (not to mention the MP2-type methods) of such complex systems as $(C_6H_5SiO_{1.5})_{12}$ are impossible, we calculated the simpler molecule **5** having replaced phenyl groups in dodecaphenylsilsesquioxane by methyl ones using the published data.[19—22] Possible calculation errors due to this replacement were estimated by comparing the results of calculations of the octamethylsilsesquioxane molecule (**4**) with the corresponding experimental geometric parameters and with the results obtained for the model molecule **4**, whose parameters were obtained by replacing phenyl groups in octaphenylsilsesquioxane by methyl ones (X-ray data for the crystal solvate with acetone).[23]

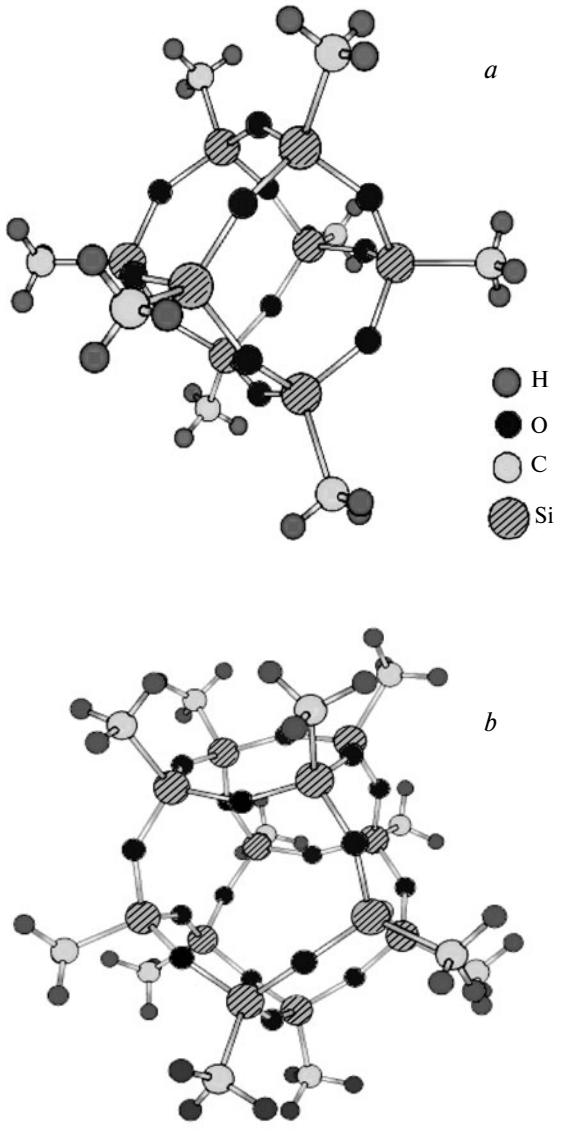

Fig. 2. Structures of sesquioxanes **4** (*a*) and **5** (*b*) determined by X-ray analysis. The plots were made using the ChemCraft software.

A similar approach was also used in the case of cage-like MOS molecules. We used X-ray data for the crystal solvates of phenyl derivatives of the sandwich $[(C_6H_5SiO_{1.5})_6]_2(CuO)_6$ (see Refs 24, 25), $[(C_6H_5SiO_{1.5})_6]_2(CuO)_4(NaO_{0.5})_4]$ (see Ref. 8), and globular $[(C_6H_5SiO_{1.5})_{12}(CuO)_4(NaO_{0.5})_4]$ MOS (see Refs 6, 26); however, phenyl groups in these molecules were replaced by methyl ones. The structures of the model sandwich $[(CH_3SiO_{1.5})_6]_2(CuO)_6$ (**1**), $[(CH_3SiO_{1.5})_6]_2(CuO)_4(NaO_{0.5})_4$ (**2**) and globular $(CH_3SiO_{1.5})_{12}(CuO)_4(NaO_{0.5})_4$ (**3**) molecules (see Fig. 1) were used in quantum chemical calculations.

Thermal destruction of cage-like MOS proceeds at temperatures higher than the temperature region corresponding to the loss of solvents; therefore, molecules **1—5** were calculated ignoring possible influence of solvation shells on their electronic structure and energy characteristics.

Molecule **1** has symmetrically arranged siloxane rings. The copper atoms form a virtually planar hexagon in the middle of the sandwich. The average distance between adjacent Cu atoms in the hexagon is 2.87 Å. Each copper atom has two siloxane ring oxygen atoms in the nearest environment.[24, 25]

In molecule **2**, in the middle of the silsesquioxane sandwich there are four Cu atoms forming an almost planar rectangle with the side lengths of 3.95 and 3.01 Å. Each Cu atom is coordinated to two oxygen atoms with nonequivalent bonds (1.88 and 1.95 Å) of the upper siloxane ring and two oxygen atoms of the lower siloxane ring. One sodium atom is symmetrically located above the upper siloxane ring, while the second sodium atom is symmetrically located under the lower siloxane ring,

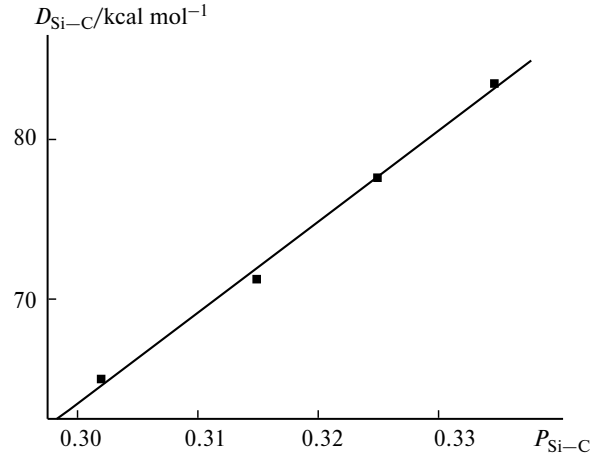

Fig. 3. Bond dissociation energies (D_{Si-C}) of methylsilanes plotted *vs.* Mulliken bond populations (P_{Si-C}). Obtained from B3LYP calculations.

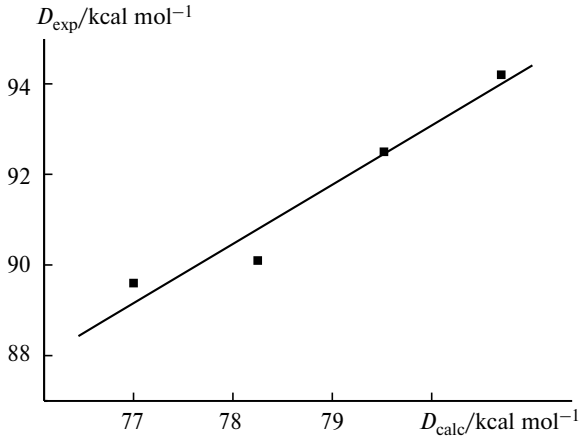

Fig. 4. Correlation between the calculated (D_{calc}) and experimental (D_{exp}) Si—C bond dissociation energies in methylsilanes.

and two remaining sodium atoms are in the same plane where the four copper atoms are located.[8] In globular molecule **3** the siloxane units form a closed twelve-membered cycle. The distance between copper atoms is rather long, 4.39 Å (see Refs 6, 26).

We calculated the total energies (E_{tot}) and the average effective atomic charges (q) of copper, silicon, oxygen, and carbon in molecules **1—5** (see Table 1).

According to calculations, the polarity of the Si—C bonds in the MOS cage is lower than that in the cage-like silsesquioxanes, whereas in the MOS cage the polarity of Si—O bonds in siloxane rings is higher than that of the Si—O bond between the siloxane rings. For instance, in molecule **1** the average atomic charge of silicon is 1.768 e, that of the siloxane ring oxygen is −0.977 e, and that of the out-of-siloxane ring oxygen is −0.900 e.

To reveal a correlation between the P_{Si-C} bond population in the organosilicon molecules and the dissociation energy of this bond (D_{Si-C}), we analyzed the dependence of the calculated Si—C bond dissociation energies on the population of this bond in a series of methylsilanes (Me—SiH_3, Me—$SiMeH_2$, Me—$SiMe_2H$, and Me—$SiMe_3$) for which experimental D_{Si-C} values are known.[27] The Si—C bond energies in silanes are calculated as the differences between the total energies of silanes and the total energies of the radicals produced upon Si—C bond dissociation (in the case of radicals, the ROB3LYP method was used). As it is seen from Fig. 3, there is a linear dependence of P_{Si-C} on D_{Si-C}, which is described by the following equation:

$$D_{Si-C} = 113.94P_{Si-C} + 42.51.$$

At the same time, from Fig. 4 it follows that all calculated and experimental values[27] of the Si—C bond energies in the considered series of methylsilanes differ by about the same value of the order of 14 kcal mol^{-1} and that there is quite good linear dependence between them. Based on this results, we estimated the Si—C bond energies in the model cage compounds **1—5**. According to calculations, the average Si—C bond population (P_{Si-C}) in molecules **1—5** is 0.374, 0.331, 0.320, 0.412 (0.440 when using the experimental geometric parameters of molecule **4** (see Ref. 19—20)), and 0.412, respectively. Assuming that for the cage-like silsesquioxanes and MOS **1—5** the dependence between the population P_{Si-C} and the bond energy D_{Si-C} is the same as for silanes (see Fig. 3), one gets the following D_{Si-C} values: 80.2, 85.1, 79.0, 89.5 (92.6), and 89.5 kcal mol^{-1}, respectively. In the cage-like MOS **1—3** the Si—C bond energies are within the interval from 79.0 to 85.1 kcal mol^{-1}; it follows that the Si—C bonds in compounds **3—5** are weaker than the corresponding bonds in the methylsilsesquioxanes.[1,2]

Although the real dependence between the Si—C bond populations and the D_{Si-C} in organosiloxanes can to some extent differ from that obtained for methylsilanes (see above), the calculated bond energies are of undoubted interest for various comparisons. They indicate that the introduction of transition metal atoms (in particular, copper) into the siloxane cage of polyorganosiloxane molecules can result in considerable changes in the Si—C bond strength at adjacent silicon atom and, correspondingly, be an important factor determining the temperature interval and the character of thermal and thermooxidative destructive transformations of these compounds.

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References

1. K. A. Andrianov, A. A. Zhdanov, *Dokl. Akad. Nauk SSSR*, 1957, **114**, 1005 [*Dokl. Chem.* (*Engl. Transl.*), 1957, **114**, No. 5].
2. K. A. Andrianov, A. A. Zhdanov, *J. Polymer Sci.*, 1958, **30**, 513.

3. N. G. Konstantinova, A. A. Zhdanov, K. A. Andrianov, in *Khimiya i practicheskoe primenenie kremniyorganicheskikh soedineniy* [*Chemistry and Practical Use of Organosilicon Compounds*], CBTI, Leningrad, 1958, **4**, 24 (in Russian).
4. K. A. Andrianov, L. M. Khananashvili, *Tekhnologiya elementoorganicheskikh monomerov i polimerov* [*Technology of Organoelement Monomers and Polymers*], Khimiya, Moscow, 1998, 528 pp. (in Russian).
5. A. A. Zhdanov, N. V. Sergienko, N. S. Trankina, *Zh. Vseros. Khim. Obshch. im. D. I. Mendeleeva*, 2001, **45**, 44 [*Mendeleev Chem. J.* (*Engl. Transl.*), 2001, **45**, No. 4].
6. V. I. Igonin, S. V. Lindeman, Yu. T. Struchkov, O. I. Shchegolikhina, A. A. Zhdanov, Yu. A. Molodtsova, I. V. Razumovskaya, *Metalloorg. Khim*, 1991, **4**, 1355 [*J. Organomet. Chem. USSR* (*Engl. Transl.*), 1991, **4**].
7. E. S. Trankina, PhD Chem. Thesis, Institute of organoelement compounds, Russian Akad. Sci., Moscow, 2003, 145 pp. (in Russian).
8. B. G. Zavin, N. V. Sergienko, E. V. Gorodnichev, V. D. Myakushev, A. A. Korlyukov, M. Yu. Antipin, *Mendeleev Commun.*, 2005, **15**, 245.
9. M. M. Levitsky, *Zh. Vseros. Khim. Obshch. im. D. I. Mendeleeva*, 2002, **46**, 51 [*Mendeleev Chem. J.* (*Engl. Transl.*), 2002, **46**, No. 3].
10. M. M. Levitsky, B. G. Zavin, A. N. Bilyachenko, *Usp. Khim.*, 2007, **76**, 907 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2007, **76**, 907].
11. A. A. Zhdanov, M. M. Levitsky, O. Yu. Shilkloper, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 958 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1985, **34**, 877].
12. M. I. Buzin, I. O. Volkov, I. I. Dubovik, E. A. Trankina, N. V. Sergienko, B. G. Zavin, V. S. Papkov, *IV All-Russia Karginskaya Conf. "The Science of Polymers to XXI Century"* (*Moscow, January 29 — February 2, 2007*), *Abstr.*, Moscow, 2007, 68.
13. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *GAUSSIAN-98, Revision A.5*, Gaussian, Inc., Pittsburgh (PA), 1998.
14. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
15. C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1988, **150**, 785.
16. M. J. Frish, J. A. Pople, J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265.
17. T. H. Dunning, Jr., P. J. Hay, in *Modern Theoretical Chemistry*, Ed. H. F. Schaefer III, Plenum Press, New York, 1976, pp. 1—28.
18. V. I. Minkin, B. Ya. Simkin, R. M. Minyaev, *Teoriya stroeniya molekul* [*The Theory of the Structure of Molecules*], Phenix, Rostov-na-Dony, 1997, 558 pp. (in Russian).
19. K. Larsson, *Ark. Kemi*, 1960, **16**, 203.
20. G. Koellner, U. Mueller, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1989, **45**, 1106.
21. W. Clegg, G. M. Sheldrick, N. Vater, *Acta Crystallogr., Sect. B: Struct. Cristallogr.*, 1980, **36**, 3162.
22. V. E. Shklover, Yu. E. Ovchinnikov, Yu. T. Struchkov, M. M. Levitsky, A. A. Zhdanov, *Metalloorg. Khim.*, 1988, **1**, 1273 [*J. Organomet. Chem. USSR* (*Engl. Transl.*), 1988, **1**].
23. M. A. Hossian, M. B. Hursthouse, K. M. Malik, *Acta Crystallogr., Sect. B: Struct. Cristallogr.*, 1979, **35**, 2258.
24. V. A. Igonin, O. I. Shchegolikhina, S. V. Lindeman, M. M. Levitsky, Yu. T. Struchkov, A. A. Zhdanov, *J. Organomet. Chem.*, 1992, **423**, 351.
25. S. V. Lindeman, O. I. Shchegolikhina, Yu. A. Molodtsova, A. A. Zhdanov, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1997, **53**, p. 305.
26. C. Bauch, L. Zherlitsyna, N. Auner, M. Bolte, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2006, **62**, 705.
27. Yu-R. Luo, *Handbook of Bond Dissociation Energies in Organic Compounds*, 2003, CRC Press, Boca Raton—London—New York—Washington, 2003.

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