ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 6, pp. 1067–1073. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © A.Yu. Timoshkin, I.V. Kazakov, C. von Hänesch, 2009, published in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 6, pp. 895–901.

Experimental and Theoretical Study on the Reactivity of Phosphorus-Containing Cubane Type Clusters $[RMPR']_4$ (M = Ga, In) toward Pyridine

A. Yu. Timoshkin[a], I. V. Kazakov[a], and C. von Hänesch[b]

[a] *St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia*
e-mail: alextim@AT11692.spb.edu

[b] *Institut für Nanotechnologie, Forschungszentrum Karlsruhe, Hermann-von-Helmholtz-Platz 1, Eggenstein-Leopoldshafen, 76344 Germany*

Received July 3, 2008

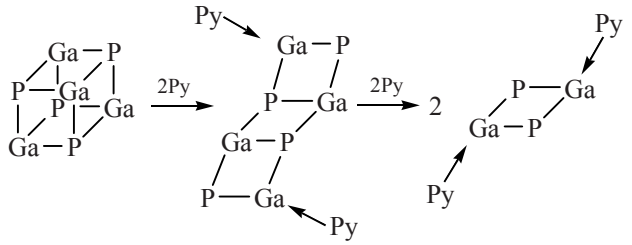
Abstract—Reactions of cubane type clusters $[EtGaPSi(Me)_2Thex]_4$ [Thex = $CMe_2(Pr\text{-}i)$] and $\{EtInP[Si(i\text{-}Bu)_3]\}_4$ with pyridine were studied. The temperature dependences of vapor pressure over individual solid compounds were measured using a membrane pressure gauge. At a temperature above 200°C the examined clusters undergo irreversible thermal decomposition due to instability of organic substituents. According to the experimental data, the cubane clusters do not react with gaseous pyridine below their decomposition temperature. Thermodynamic parameters for the isomerization of model clusters $[HMPH]_4$ (M = Ga, In) and their gas-phase reactions with pyridine were calculated by quantum-chemical methods. The addition of pyridine is thermodynamically allowed only at low temperatures.

DOI: 10.1134/S1070363209060048

Binary and composite phosphides derived from Group 13 elements are widely used in microelectronics. Promising initial compounds for their synthesis are oligomeric structures, in particular tetrameric clusters like $[RMPR']_4$. Up to now, more than 40 compounds derived from Groups 13–15 elements and having cubane type structure with an M_4Y_4 skeleton (where M is a Group 13 element, and Y is a Group 15 element) have been synthesized, and their structure have been determined [1]. All these compounds contain bulky substituent R or R′. The calculated structural and thermodynamic parameters of model compounds $[XMYH]_4$ (M = Al, Ga, In; Y = N, P, As; X = H, F, Cl, Br, I) were given in [2]. As shown in [3], mixed heterometallic cubane type clusters (i.e., those containing different metal atoms) are characterized by almost the same stability as homometallic clusters.

Thermal behavior and reactivity of tetrameric $[RMPR']_4$ compounds have been studied poorly; therefore, measurement of their vapor pressure and determination of their thermal stability limit constitute important problems. In some cases, the synthesis of cubane type clusters in nonaqueous solution was accompanied by formation of stair-like structures stabilized by two molecules of donor solvent (Et_2O [4, 5] or PR_3 [6]), so that the reactivity of cubane type clusters toward donor molecules is also an important factor.

The possibility for decomposition of the cubane type skeleton to give stair-like structure by the action of strong Lewis acids was studied using the reaction with pyridine as an example. Such process for the $[RGaPR']_4$ cluster is illustrated by the scheme shown below.



For the sake of clarity, organic substituents R and R′ on the gallium and phosphorus atoms are not shown. In the first step, dissociation of two Ga–P bonds in the cubane type skeleton is possible with formation of stair-like structure stabilized by two

pyridine molecules. In the second step (provided that excess pyridine is present), further addition of donor molecules can occur with cleavage of the Ga–P bonds and formation of $[RGaPR']_2 \cdot 2Py$ dimers stabilized by dative bonds. Analogous dimers are well known; for example, $[ClAlPSi(i\text{-}Pr_3)]_2 \cdot 2Py$ was synthesized and structurally characterized in [5].

In the present work we were the first to study by experimental and theoretical methods thermal stability of phosphorus-containing gallium and indium cubane type clusters and their reactivity toward pyridine as donor ligand.

Quantum-chemical calculations were performed at the St. Petersburg State University using Gaussian 03 software package [7] in terms of the density functional theory {Becke three-parameter exchange functional with Lee–Yang–Parr correlation functional B3LYP [8, 9]; LANL2DZ(*d*,*p*) basis set [10] supplemented by polarizing functions as described in [11, 12]}. The geometric parameters were optimized so that the resulting structures occupied minima on the potential energy surfaces. Figures 1 and 2 show the optimized structures of model gallium-containing compounds. Indium compounds have analogous structures.

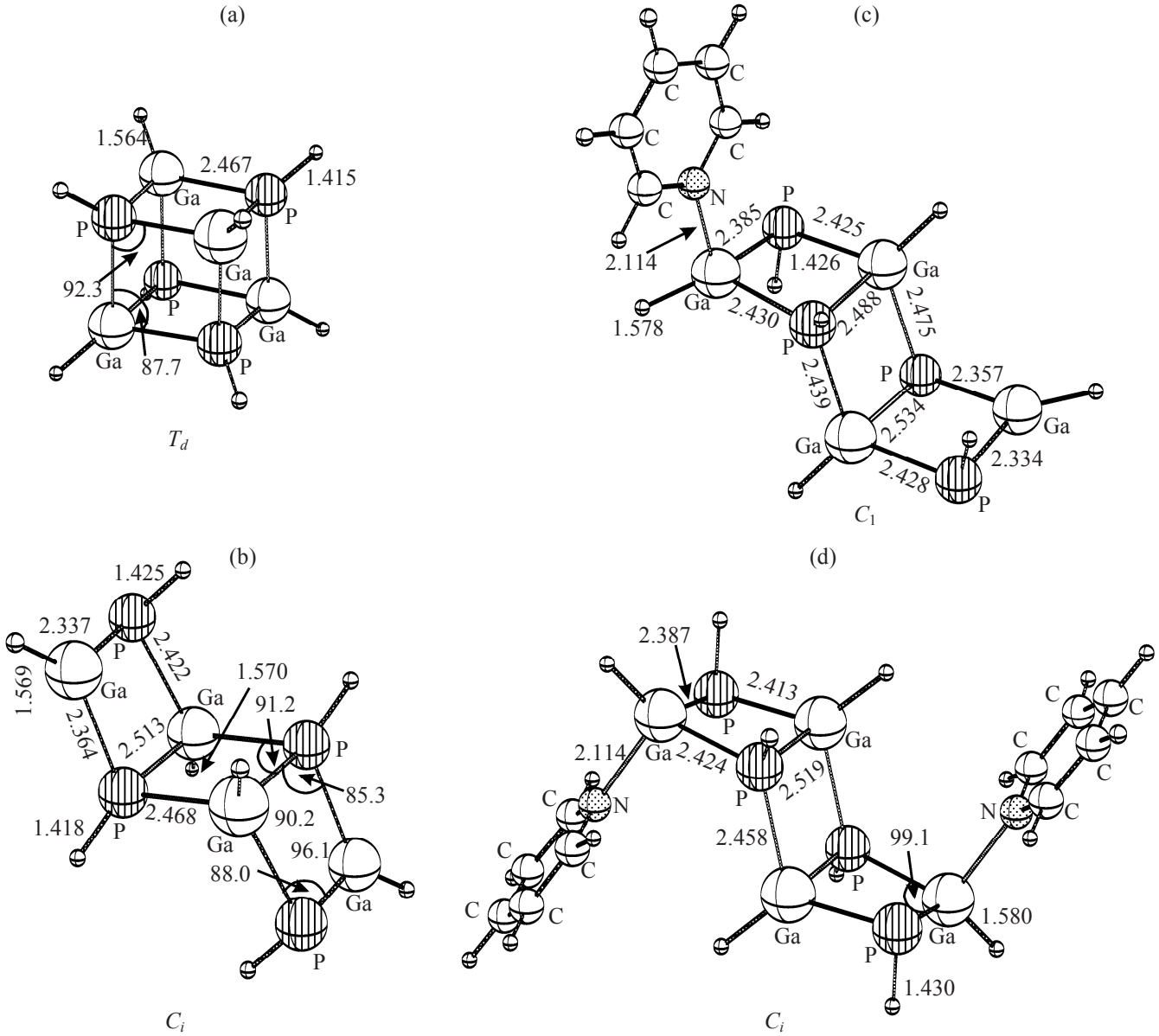


Fig. 1. Optimized [B3LYP/LANL2DZ(*d*,*p*)] structures of $[HGaPH]_4$ and its complexes with pyridine. The bond lengths are given in Å, and the bond angles, in degrees. (a) Cubane-type $[HGaPH]_4$; (b) stair-like $[HGaPH]_4$; (c) stair-like $[HGaPH]_4 \cdot Py$; (d) stair-like $[HGaPH]_4 \cdot 2Py$.

Model cubane type cluster $[HGaPH]_4$ (Fig. 1a) is characterized by high symmetry (T_d point group symmetry); the Ga–P bonds are absolutely equivalent (2.467 Å). Cleavage of two Ga–P bonds gives centrosymmetric stair-like isomer (Fig. 1b) in which four central atoms in the Ga_2P_2 ring retain their coordination number (4), while the coordination number of four terminal atoms changes to 3. This is accompanied by considerable change in the Ga–P bond lengths: the Ga–P bonds between the three-coordinate atoms are shorter by 0.13 Å than those in the initialo cubane type structure. In addition, the terminal phosphorus atoms become strongly pyramidalized. Due to shortening of the terminal bonds and pyramidalization of the phosphorus atoms the stair-like isomer is less stable than the initial cubane type structure by only 74 (M = Ga) or 96 kJ mol^{-1} (M = In) despite cleavage of two metal–phosphorus bonds.

Cleavage of four Ga–P bonds in the initial cubane type structure leads to the formation of coordinately unsaturated dimers $[HMPH]_2$ which may have C_{2h}

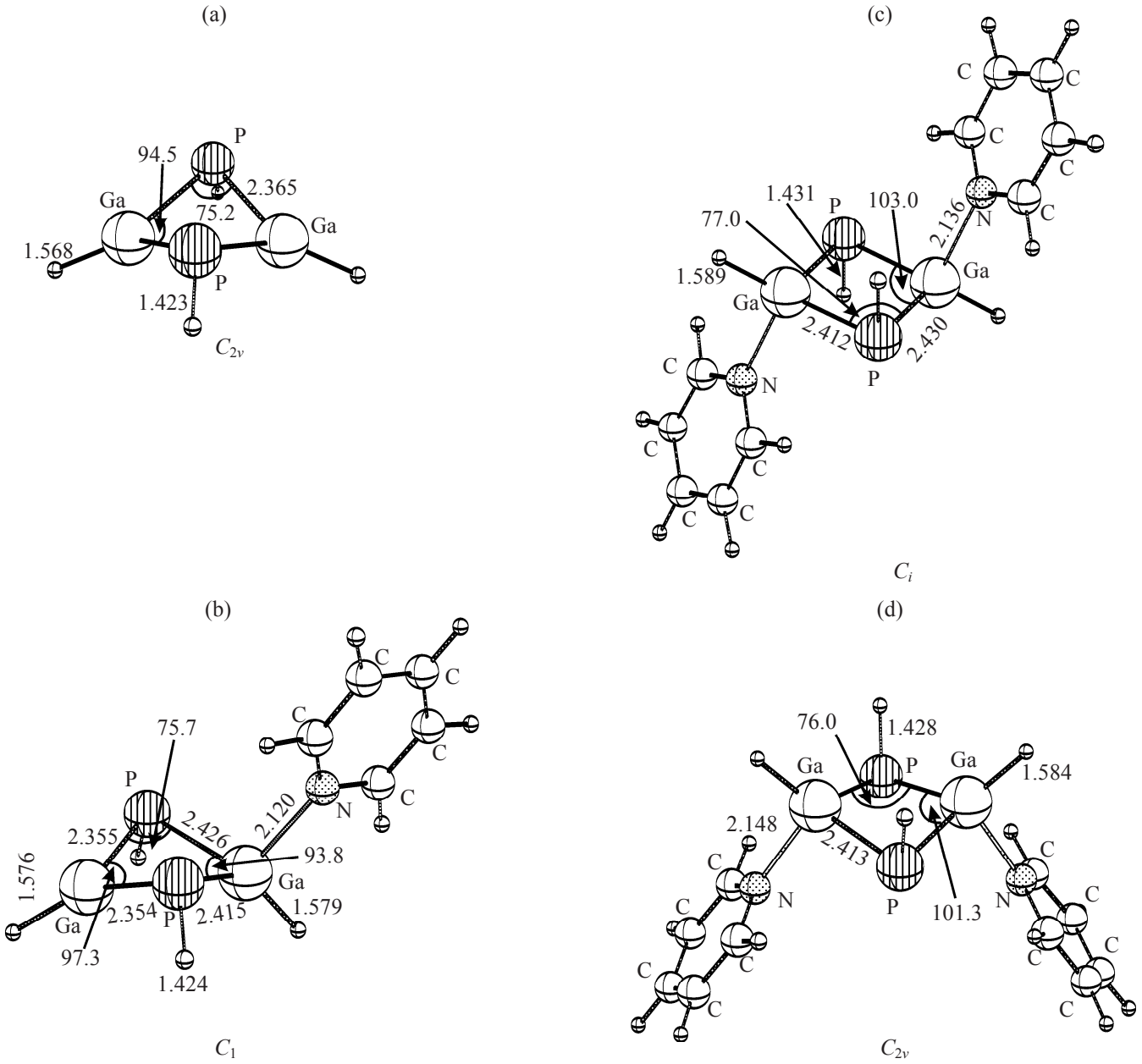


Fig. 2. Optimized [B3LYP/LANL2DZ(*d*,*p*)] structures of $[HGaPH]_2$ and its complexes with pyridine. The bond lengths are given in Å, and the bond angles, in degrees. (a) *cis*-$[HGaPH]_2$, (b) *cis*-$[HGaPH]_2 \cdot Py$; (c) *trans*-$[HGaPH]_2 \cdot 2Py$; (d) *cis*-$[HGaPH]_2 \cdot 2Py$.

structure with planar Ga_2P_2 ring and C_{2v} structure with distorted Ga_2P_2 ring. The latter (Fig. 2a) is more stable by 12 (M = Ga) or 8 kJ mol^{-1} (M = In).

The calculated thermodynamic parameters of the gas-phase processes are given in table. Addition of each pyridine molecule at the terminal atom M in the stair-like structure is accompanied by an energy gain of 84 to 98 kJ mol^{-1}. Thus addition of two pyridine molecules completely compensates the energy consumed for cleavage of Ga–P bonds and skeletal reorganization from the cubane to star-like structure.

The addition of pyridine molecules occurs independently, as follows from similar energies of complex formation with the first and second pyridine molecules, as well as from similarity of the metal–nitrogen bonds in the complexes $[HGaPH]_4 \cdot Py$ and $[HGaPH]_4 \cdot 2Py$. The complex formation is an exothermic process but is unfavorable by entropy. Therefore, the temperature at which the equilibrium constant is equal to unity ($T_{K=1}$) is very low, and the formation of $[HGaPH]_4 \cdot Py$ and $[HGaPH]_4 \cdot 2Py$ becomes thermodynamically unfavorable above 207 and 454 K, respectively.

Further addition of pyridine molecules with formation of dimer complexes is possible only below 350 K. Of the two possible $[HMPH]_2 \cdot 2Py$ isomers, the *cis* structure (Fig. 2d) is more stable than *trans* (Fig. 2c) by 11 (M = Ga) and 9 kJ mol^{-1} (M = In); therefore, only thermodynamic parameters for the formation of most stable *cis* isomers are given in table. The reverse process, i.e., the formation of cubane type structure ($2cis$-$[HGaPH]_2 \cdot 2Py \rightarrow [HGaPH]_4 + 4Py$) is thermodynamically allowed above 350 K; the corresponding temperature limit for the indium-containing analog is as low as 200 K. Thus the calculation showed that complex formation with pyridine is thermodynamically favorable only at low temperatures.

Experimental studies were performed with $[EtGaPSi(Me)_2Thex]_4$ [Thex = CMe_2(*i*-Pr) (**I**) and $[EtInPSi(i\text{-}Bu_3)]_4$ (**II**). Preliminarily, we measured the temperature dependences of vapor pressure over pure compounds **I** and **II**. The vapor pressure over the solid

Calculated [B3LYP/LANL2DZ(*d*,*p*)] thermodynamic parameters of gas-phase processes

Process	ΔH^0_{298}, kJ mol^{-1}	ΔS^0_{298}, J mol^{-1} K^{-1}	ΔG^0_{298}, kJ mol^{-1}	ΔG^0_{500}, kJ mol^{-1}	$T_{K=1}$, K
Gallium clusters					
$[HGaPH]_4 \rightarrow$ stair-like $[HGaPH]_4$	74.1	70.5	53.1	38.9	1051
$[HGaPH]_4 + Py \rightarrow$ stair-like $[HGaPH]_4 \cdot Py$	–18.1	–87.4	7.9	25.5	207
$[HGaPH]_4 + 2Py \rightarrow$ stair-like $[HGaPH]_4 \cdot 2Py$	–116.0	–255.6	–39.8	11.8	454
$[HGaPH]_4 \rightarrow 2\,cis$-$[HGaPH]_2$	177.8	226.7	110.2	64.4	784
cis-$[HGaPH]_2 + Py \rightarrow [HGaPH]_2 \cdot Py$	–84.1	–149.9	–39.4	–9.2	561
cis-$[HGaPH]_2 + 2Py \rightarrow cis$-$[HGaPH]_2 \cdot 2Py$	–154.6	–301.5	–64.8	–3.9	513
$[HGaPH]_4 + 4Py \rightarrow 2\,cis$-$[HGaPH]_2 \cdot 2Py$	–131.5	–376.3	–19.3	56.6	350
Indium clusters					
$[HInPH]_4 >$ stair-like $[HInPH]_4$	95.1	75.7	72.5	57.2	1256
$[HInPH]_4 + Py \rightarrow$ stair-like $[HInPH]_4 \cdot Py$	11.2	–78.8	34.7	50.6	–
$[HInPH]_4 + 2Py \rightarrow$ stair-like $[HInPH]_4 \cdot 2Py$	–78.1	–240.3	–6.5	42.1	325
$[HInPH]_4 \rightarrow 2\,cis$-$[HInPH]_2$	222.0	232.2	152.8	105.9	956
cis-$[HInPH]_2 + Py \rightarrow [HInPH]_2 \cdot Py$	–78.8	–147.2	–34.9	–5.2	535
cis-$[HInPH]_2 + 2Py \rightarrow cis$-$[HInPH]_2 \cdot 2Py$	–147.6	–299.0	–58.5	1.9	494
$[HInPH]_4 + 4Py \rightarrow 2\,cis$-$[HInPH]_2 \cdot 2Py$	–73.2	–365.8	35.8	109.7	200

samples of **I** and **II** at 150°C was insignificant (less than 5 mm). Both compounds are stable under these conditions. Their slow decomposition started at ~200°C.

No increase in the overall vapor pressure was observed when cluster **I** was kept for 1 h at 200°C (vapor pressure 8 mm), whereas prolonged heating at that temperature was accompanied by slow decomposition. Heating of cluster **II** for 13.5 h at 198–203°C resulted in increase of the overall vapor pressure by 1 mm, i.e., by a value appreciably exceeding the experimental error. Irreversible thermal decomposition occurred at an appreciable rate on heating to 235–240°C. Low vapor pressure and narrow temperture range (limited by nonequilibrium thermal dissociation) did not allow us to determine thermodynamic parameters for vaporization of **I** and **II**.

The reaction with pyridine was studied as follows. A 24.37-ml reactor was charged with a small amount of pyridine (14.6 mg), and the temperature dependence of vapor pressure of pure pyridine was measured. The *P*–*T* plot is shown in Fig. 3. The ratio $P/T = (m/M)(R/V)$ is proportional to the concentration of pyridine in the system. At 78°C, the entire amount of pyridine is transferred to the gas phase, and further change in its pressure with temperature conforms to its thermal expansion (P/T = const). The data obtained for two successive heating–cooling cycles are very consistent, indicating that the results are reproducible.

After two heating–cooling cycles, a 0.946-ml ampule containing 119.1 mg of compound **I** was opened within the reactor, the system was kept for several hours at room temperature, and the vapor pressure was measured while continuously heating at a rate of 0.5–1 deg min^{-1}. Taking into account that the ratio of pyridine to compound **I** was 1.68 : 1, the formation of a complex with pyridine should be accompanied by considerable decrease in pressure. However, the experimental data (Fig. 3) indicated the opposite.

At high temperature, the P/T ratio in the system compound **I**–pyridine (with account taken of increase in the volume after opening of the ampule with **I**) was even greater than the P/T ratio for pure pyridine. We believe that the difference may be attributed to "parasite pressure" which appears while weighing a sample of **I** (see Experimental). In fact, the P/T value for the system compound **I**–pyridine at low temperature is greater than P/T for saturated vapor of pure pyridine. The vapor pressure in the system **I**–Py was measured during three successive heating–cooling

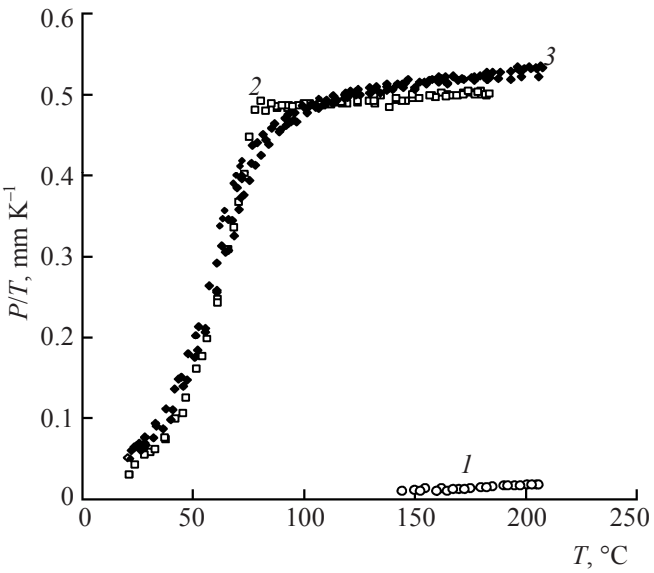


Fig. 3. Plots of the P/T ratio (mm K^{-1}) versus temperature (°C) for (*1*) individual compound **I**, (*2*) pyridine, and (*3*) **I**–Py.

cycles. The results were generally consistent; however, each subsequent heating–cooling cycle was accompanied by a slight increase in P/T, presumably due to partial decomposition.

In the region near the transition point to unsaturated vapor, the saturated vapor pressure in the system **I**–Py is considerably lower than the saturated vapor pressure of pure pyridine. This deviation originates from dissolution of cluster **I** in liquid pyridine (a yellowish solution over crystalline compound was observed by the end of experiment). The P/T values in the region corresponding to unsaturated vapor indicate that no interaction occurs between compound **I** and pyridine in the examined temperature range.

Analogous experiments were performed with the system compound **II**–pyridine [pyridine sample weight 56 mg, compound **II** sample weight 200 mg, system volume 39.53 ml, volume of the tube with compound **II** 2.16 ml, ratio pyridine–compound **II** 4.75 : 1]. Likewise, no interaction between $[EtInPSi(i\text{-}Pr_3]_4$ and pyridine was observed (Fig. 4).

We can conclude that cubane-type clusters **I** and **II** do not react with pyridine below their decomposition temperature. This is consistent with the results of quantum-chemical calculations on the reactivity of **I** and **II** toward pyridine. Their low reactivity at reduced temperature may be related to the effect of blky organic substituents which hamper attack by the donor molecule.

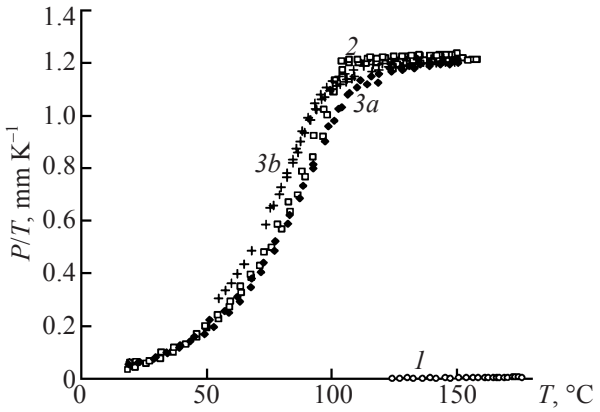


Fig. 4. Plots of the P/T ratio (mm K^{-1}) versus temperature (°C) for (*1*) individual compound **II**, (*2*) pyridine, and (*3*) **II**–Py; (a) heating and (b) cooling.

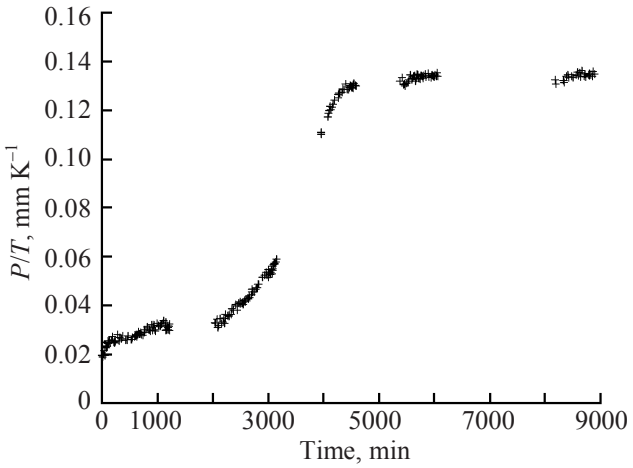


Fig. 5. Plot of the P/T ratio (mm K^{-1}) versus time (min) for individual compound **II** on heating at 227 ± 10°C.

We also examined thermal decomposition of individual compound **II**. The overall pressure in the system considerably increased with time on heating at 227 ± 10°C over a period of ~150 h. Figure 5 shows the P/T plot versus time, which is an *S*-shaped curve typical of autocatalytic processes. The system was then cooled with liquid nitrogen (the vapor pressure was ~2 mm), and the vapor pressure was measured as the temperature rose. A sharp increase in pressure was observed in the temperature range from –100 to –60°C; these findings indicate that the main decomposition products are gaseous substances which condense at the temperature of liquid nitrogen.

EXPERIMENTAL

Compounds **I** and **II** were synthesized as described in [13, 14], traces of solvent were removed by continuous evacuation over a period of 2 h, and the compounds were placed into ampules which were sealed under reduced pressure. Both substances were colorless powders which turned yellowish on heating. Taking into account high hygroscopicity of compounds **I** and **II**, all operations were performed in preliminarily evacuated jointless glassware, which completely excluded contact with atmospheric oxygen and moisture. Because of low volatility and thermal instability, compounds **I** and **II** were packed into ampules by pouring in evacuated glass systems. In doing so, a thin layer of substance remains at the place where the ampule is sealed off. As a result, a part of a substance undergoes decomposition which produces a small parasite pressure. Therefore, in each heating–cooling cycle of individual compounds **I** and **II**, the parasite pressure calculated by averaging P/T values in the initial period with account taken of thermal expansion was subtracted from the overall pressure.

Pyridine was preliminarily purified by distillation under reduced pressure to remove dissolved gases. It was then purified by keeping over preliminarily calcined NaA and CaA zeolites, and its purity was checked by gas chromatography on a Tsvet-560 chromatograph.

Mass spectrometric study on compounds **I** and **II** (MKh-1321 instrument; electron impact, 70 eV) revealed their appreciable volatility at 170°C. The P–T dependences were measured by the static method using a glass membrane pressure gauge [15]. The setup was made of molybdenum or quartz glass. The pressure was measured with an MChR-3 manometer with an accuracy of ±0.1 mm. The temperature was controlled using two chromel–alumel thermocouples with an accuracy of ±0.05°C, and the thermoelectromotive force was measured using a Shch-1516 digital voltmeter. The volume of the membrane chamber was determined from the weight difference between the empty system and that filled with water; the error in the volume measurement was ±0.02 ml (0.1% for a ~20-ml setup).

ACKNOWLEDGMENTS

The authors thank A.D. Misharev for recording the mass spectra.

REFERENCES

1. Timoshkin, A.Y., *Coord. Chem. Rev*., 2005, vol. 249, p. 2094.
2. Timoshkin, A.Y. and Schaefer, H.F., *Inorg. Chem*., 2004, vol. 43, p. 3080.
3. Timoshkin, A.Y., *Solid State Electronics*, 2003, vol. 47, p. 543.
4. von Hänisch, C. and Weigend, F., *Z. Anorg. Allg. Chem*., 2002, vol. 628, p. 389.
5. von Hänisch, C., *Z. Anorg. Allg. Chem*., 2003, vol. 629, p. 1496.
6. von Hänisch, C., Scheer, P., and Rolli, B., *Eur. J. Inorg. Chem*., 2002, p. 3268.
7. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, J.A., Jr., Vreven, T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonzalez, C., and Pople, J.A., *Gaussian 03, Revision B.01*, Pittsburgh, PA: Gaussian, 2003.
8. Becke, A.D., *J. Chem. Phys*., 1993, vol. 98, p. 5648.
9. Lee, C., Yang, W., and Parr, R.G., *Phys. Rev. B*, 1988, vol. 37, p. 785.
10. Hay, P.J. and Wadt, W.R., *J. Chem. Phys*., 1985, vol. 82, p. 270.
11. Timoshkin, A.Yu., Suvorov, A.V., and Shefer, G.F., *Russ. J. Gen. Chem*., 1998, vol. 68, p. 1138.
12. Timoshkin, A.Y., Suvorov, A.V., Bettinger, H.F., and Schaefer, H.F., *J. Am. Chem. Soc*., 1999, vol. 121, p. 5687.
13. von Hänisch, C. and Rolli, B., *Phosphorus, Sulfur Silicon Relat. Elem*., 2004, vol. 179, p. 749.
14. von Hänisch, C. and Rolli, B., *Z. Anorg. Allg. Chem*., 2002, vol. 628, p. 2255.
15. Suvorov, A.V., *Termodinamicheskaya khimiya paroobraznogo sostoyaniya* (Thermodynamic Chemistry of the Gas Phase), Leningrad: Khimiya, 1970.