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An Insight into the Structure of Model Germaphosphaallenes

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The geometries of all possible isomers of the model compound $\text{H}_2\text{Ge}=\text{C}=\text{PH}$ were optimized at the B3LYP/6-31G(d,p) level of the theory. The calculation was repeated at higher correlated methods with similar results and for the isomers of the methyl-substituted phosphagermaallene $\text{MeP}=\text{C}=\text{GeMe}_2$. As another way to stabilise the $\text{P}=\text{C}=\text{Ge}$ unit consists in the use electronic effects, a NBO study was carried out in order to identify the influence that the nature (electropositive or electronegative) of several substituents would have on the strength of the $\text{C}=\text{Ge}$ bond. Model compounds $\text{HP}=\text{C}=\text{GeR}_2$ and $\text{HP}=\text{C}=\text{GeRR}'$ were investigated ($\text{R} = \text{BH}_2, \text{CH}_3, \text{SiH}_3, \text{NH}_2, \text{OMe}, \text{F}$; $\text{R}' = \text{H}$). It was found that the main interaction contributing to the weakening of the $\text{C}=\text{Ge}$ bond is a transfer of electron density from the lone pair of the phosphorus atom to the molecular antibonding orbital localized on the $\text{Ge}-\text{C}$ bond.

Keywords: phosphagermaallenes, B3LYP, CCSD, MP4, theoretical study

I. Introduction

The chemistry of allene analogues of group 14 elements has been in the focus of the scientific community for more than three decades, since the synthesis of the first silaallene by Brook *et al.* [1]. Our group has been interested mainly in the synthesis, characterizations and reactivity of phosphaaallenes in which one of the carbon atom is formally replaced with heavy group 14 elements, like Si, Ge and Sn [2-4].

A general synthetic route towards phosphagermaallene has been established by our group [3] and it includes the dehalogenation of 2,3-dihalo-1-phospha-3-germa-1-propenes by means of a lithium reagent. While several precursors of this type have been synthesized [5, 6], the choice of the appropriate organic groups on both the phosphorus and the germanium atoms plays an important role in the outcome of the reaction, as it has been shown by us previously [7, 8, 9].

A transient phosphagermaallene [8] has been evidenced and the synthesis of the first stable phosphagermaallene, $\text{Mes}^*\text{P}=\text{C}=\text{Ge}(t\text{Bu})(\text{Tip})$ ($\text{Mes}^* = 2, 4, 6\text{-tri-}i\text{-tert-butyl-phenyl}$, $\text{Tip} = 2, 4, 6\text{-tri-}i\text{-propyl-phenyl}$) has been carried out recently by our group [9]. These compounds have been characterized through the usual spectroscopic methods (NMR, IR), but their instability makes computational chemistry a useful tool in the study of their structure and properties, providing the means to investigate them. However, there is only a limited number of papers dealing with theoretical aspects of phosphagermaallenes chemistry. Thus, Escudié *et al.* rationalized [8] the dimerization outcome of $\text{Mes}^*\text{P}=\text{C}=\text{GeMe}_2$. Their RHF study shows that, the

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head-to-head dimerization of two Ge=C bonds is favoured, in contrast with the experimentally observed formation of four-atom rings from head-to-tail dimerization involving two double Ge=C bonds or a head-to-tail P=C and a Ge=C dimerization (forming new P-C and Ge-C bonds) [8]. Note however that the most important calculated difference in energy between the head-to-head and head-to-tail dimers was around 24 kJ/mol. Due to the experimental use of very bulky mesityl (2,4,6-tri-methyl-phenyl) and supermesityl groups, the discrepancy with the model calculations is not surprising since the large steric hindrance of substituents disfavor the head-to-head dimers.

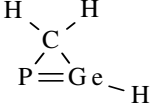
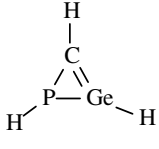
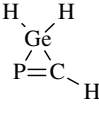
In the present work, a theoretical study on model compounds of phosphagermaallenes has been carried out, in order to further characterize such derivatives and also to rationalize the small number of such derivatives described to date.

II. Results and discussions

II.1. Structural minima of model 1-3-phosphagermaallenes – a B3LYP/6-31G(d,p) study

The geometries of all possible isomers of the model compound PCGeH₃ were optimized at the B3LYP/6-31G(d,p) [10-13] level of the theory, using the Spartan package of programs [14]. A vibrational analysis was also carried out in order to ensure that all the geometries found correspond to minima. The triplet state of the phosphagermaallene was also investigated in order to see whether the preference for the single state is kept while going from >Ge=C< to >Ge=C=P- skeletons. The energy data and results relevant geometrical parameters are given in Table 1.

Table 1. Calculated B3LYP/6-31G(d,p) energies relative to **IX** (kJ/mol) and geometrical parameters for HP=C=GeH₂ isomers (total energy of **IX** is -2458.00001 a.u.)

Molecule	HP=C=GeH ₂ I	HP=C=GeH ₂ I_t (triplet state)	Molecule	P≡C-GeH ₃ II	 III
Relative energy	195.14	285.10	Relative energy	65.28	126.25
Ge-C (pm)	177.9	186.8	Ge-C (pm)	192.2	195.3
P-C (pm)	164.1	1.650	P-C (pm)	155.3	198.8
Ge-C-P (°)	156.71	159.18	Ge-C-P (°)	179.81	65.002
Molecule	 IV	HP=Ge=CH ₂ V	Molecule	H ₂ P-C≡GeH VI	 VII
Relative energy	104.59	110.50	Relative energy	228.00	90.74
Ge-C (pm)	198.9	179.6	Ge-C (pm)	180.9	192.4
P-Ge (pm)	3.109	214.9	P-C (pm)	167.0	168.3
P-Ge-C (°)	29.427	150.00	Ge-C-P (°)	178.13	79.9

Molecule	H ₂ P-Ge≡CH VIII	P≡Ge-CH ₃ IX
Relative energy	233.68	0
Ge-C (pm)	172.7	196.7
P-Ge (pm)	235.9	202.4
P-Ge-C (°)	122.19	179.897

Thus, the following trend among the relative energies of isomers of H₃PCGe is observed (Figure 1):

Figure 1. Relative energies (compared to the series minimum **IX**) of H₃PCGe isomers

Unexpectedly, the most stable isomer is **IX**, containing the P≡Ge triple bond. This comes as a surprise, considering that the instability of multiple bonded germanium derivatives usually increases with the degree of unsaturation, and the isomer containing the P=Ge bond is thermodynamically less stable than **IX**. In fact, our results are in agreement with previous calculations data on organometallic compounds, where phosphorus-germanium triple bonds are computed to be energetically more favored than the germanium-phosphorus double bonds [15, 16]. Electronegative substituents on the germanium atom increase the strength of the triple bond, while those with lower electronegativity weaken it. The reason for which triple bonded germanium compounds are so scarce (and there are no known derivatives containing the P≡Ge unit reported up to date) must be of kinetical nature; as the use of bulky substituents providing a proper steric protection could lead to the isolation of such derivatives.

Since experimentally we start from the P=C-Ge skeleton to synthesize 1-3-phosphagermaallenes, we were more interested in the isomers containing the P-C-Ge sequence. The phosphagermirene **IV** is theoretically more likely to form than the phosphagermaallene **I**, but no such compound has been previously reported so far. The difference of about 83.74 kJ/mol between the energies of **V** and **I** can be easily covered by the ring opening of the cycle to afford the linear structure.

From all the model-compounds given in Table 1, only **VII** has a precedent [17] in the literature to be characterized by X-ray crystallography (**VIIa**), and the present DFT method affords very close geometrical parameters (see Scheme 1), indicating that this computational method is accurate enough in describing such derivatives.



Scheme 1. Bond lengths for **VII** (calculated) and **VIIa** (obtained from X-ray data)

The bent geometry obtained for **I** is not surprising for such compounds, since heavier group 14 elements are known to prefer a bent structure when involved in multiple bonding [18]. This is in sharp contrast however with the geometry of $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ allene and heavier analogues resulted by substitution of carbon for silicon, or germanium ($\text{H}_2\text{Si}=\text{Si}=\text{SiH}_2$, $\text{H}_2\text{Ge}=\text{Ge}=\text{GeH}_2$, $\text{H}_2\text{Si}=\text{C}=\text{GeH}_2$, $\text{H}_2\text{Ge}=\text{C}=\text{GeH}_2$) which are all optimized to a linear skeleton at the B3LYP/6-31G(d) method. A molecular orbital analysis of **I** reveals that the frontier orbitals have a pronounced antibonding character between the phosphorus and carbon atom in the $\text{P}=\text{C}=\text{Ge}$ unit. The HOMO is mainly localized on the $\text{Ge}=\text{C}$ double bond (Figure 2).

Figure 2. HOMO (a) and LUMO (b) orbitals of $\text{H}_2\text{Ge}=\text{C}=\text{PH}$ **I**

The same shapes of the frontier orbitals are also found for all the other isomers, the HOMO being mainly localized on the $\text{Ge}-\text{C}$ bond, while the LUMO has an even more pronounced antibonding character (with three nodal planes) and is localized on the $\text{P}-\text{C}$ fragment. The HOMO-LUMO separation for **I** is more than 4 eV. This gap is smaller for the cyclic structures **III** and **IV** (3 eV), but increases again for **VII**, which indicates that the isolation of **VIIa** is partially due to its smaller kinetical liability compared to the other isomeric rings. The use of sterically hindering substituents on the germanium and phosphorus atoms should afford the stabilization needed for the linear structure. With this in mind, we have slightly increased the steric congestion on the $\text{P}-\text{C}-\text{Ge}$ unit, performing calculations on the isomers of the model phosphagermaallene $\text{MeP}=\text{C}=\text{GeMe}_2$ at the same DFT level. The results are given in Table 2.

Table 2. Calculated B3LYP/6-31G(d,p) parameters for $\text{MeP}=\text{C}=\text{GeMe}_2$ isomers. Energies (kJ/mol are given relative to lowest calculated total energy for isomer **II** (-2575.95922 a.u.).

Molecule	I-Me₃	I_r-Me₃ (triplet)	Molecule	II-Me₃	III-Me₃
Relative energy	137.60	230.95	Relative energy	0.00	110.54
Ge-C (pm)	177.1	188.3	Ge-C (pm)	194.2	196.8
P-C (pm)	163.8	164.6	P-C (pm)	155.6	201.6
Ge-C-P (°)	167.478	157.945	Ge-C-P (°)	179.837	64.457
Molecule	IV-Me₃	V-Me₃	Molecule	VI-Me₃	VII-Me₃

Relative energy	74.48	115.44	Relative energy	174.95	35.37
Ge-C (pm)	199.7	187.4	Ge-C (pm)	183.4	193.3
P-Ge (pm)	3.070	217.6	P-C (pm)	164.2	169.8
P-Ge-C (°)	30.709	123.202	Ge-C-P (°)	158.911	79.415
<hr/>					
Molecule	VIII-Me ₃	IX-Me ₃			
Relative energy	89.55	31.37			
Ge-C (pm)	175.2	202.6			
P-Ge (pm)	240.7	202.9			
P-Ge-C (°)	105.366	179.999			

It can be noticed that the most stable isomer is isomer **II**, but that the more sterically hindered MeP=C=GeMe₂ **I-Me** is more stable by comparison with the HP=C=GeH₂ analogue, the energy difference between **I** and **IX** being 195.27 kJ/mol for the former and 105.97 kJ/mol for the latter. This is in line with the experimental observation that increasing hindrance around the Ge=C=P unit by using very bulky groups (like Mes, Tip, *t*Bu or Mes*) affords longer lifetime to allow the isolation of phosphagermaallenes [9].

There are no significant changes in the form of the frontier orbitals going from H₂Ge=C=PH to Me₂Ge=C=PMe proving that the basic electronic effects are those determined by the H₂GeCPH skeleton

II.2. Investigations of model phosphagermaallenes isomers through higher level correlation methods

To improve the treatment of electron correlation, and to check the validity of the DFT treatment geometry optimizations have also been run at the CCSD/6-31G(d, p) [19-22] and MP4(SDQ)/6-31G(d, p) [23] levels of the theory using Gaussian 98 [24]. The calculated energies are given in Table 3.

Table 3. Calculated CCSD/6-31G(d, p) and MP4/6-31G(d, p) energies (a.u.) for the phosphagermaallene isomers **I-IX**

Molecule	I	I_t triplet	II	III	IV
CCSD/6-31G(d,p)	-2453.83907	-2453.72529	-2453.89820	-2453.86917	-2453.86749
MP4/6-31G(d,p)	-2453.83852	-2453.72482	-2453.89877	-2453.86794	-2453.86626
Molecule	V	VI	VII	VIII	IX
CCSD/6-31G(d,p)	-2453.86956	-2453.81166	-2453.88406	-2453.82308	-2453.91630
MP4/6-31G(d,p)	-2453.86851	-2453.80834	-2453.88359	-2453.81987	-2453.91620

The correlation methods give similar geometries and relative energies (see the *Supplementary Information*) to those found by DFT, as isomer **IX** is calculated to be the most stable one. However the cyclic structures have lower relative energies than those calculated at the B3LYP level. It is worth to note here that the DFT methods (particularly B3LYP also) predict lower

energy for $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ than for the propyne isomer ($\text{HC}\equiv\text{C}-\text{CH}_3$ [25, 26] in contrast with experiment and results obtained at explicitly correlated methods (MP2 and CCSD(T)) with various basis sets [26]. The present B3LYP calculations on the heavier allene type systems supported by the results at the CCSD and MP4 levels increase the reliability of the DFT-B3LYP method in describing the properties of such systems.

II.3. The influence of substituents on Ge - a measure for the stability of the P=C=Ge unit

The role of electronic effects of substituents in stabilizing systems containing the P=C=Ge unit has not been assessed so far. If voluminous ligands (which block or decrease the reactivity of the protected double bond) could be replaced by smaller substituents inducing electronic stabilization (i.e. larger HOMO-LUMO gaps) the properties of this allenic core could be (at least in theory) tuned by using different types of substituents.

This study aims to identify the influence that the nature (electron withdrawing or releasing) of several substituents would have on the strength of the C=Ge bond in the P=C=Ge unit. The analysis is based on a treatment using the NBO 3.1 program [27] incorporated in Gaussian 98.

The C=Ge and C=P bond lengths found for $\text{H}_2\text{Ge}=\text{C}=\text{PH}$ by a B3LYP/6-311G(d,p) geometry optimization are 178 pm and 1.64 pm, respectively. These values are in agreement with experimental data: a 178 pm bond length was reported for Ge=C in a 1-germaallene [28]. The P=C bond in phosphallenes is usually slightly shorter than 164 pm, as expected from the *sp* hybridization of the C atom [2]. The P=C=Ge unit in the model compound is not linear, as it is the case for carbon-allenic structures; the GeCP angle has a value of 160.4°. The NBO analysis performed on the optimized structure **I** indicates a *sp* hybridization for the carbon atom, together with the expected *sp*² hybridization for the germanium. The reason for the calculated deviation from linearity seems to be an hyperconjugation effect involving donation of electron density from the phosphorus lone pair to the antibond orbital localized on the Ge-C bond (Figure 3a). This is shown by the second order perturbation analysis of the Fock matrix in the NBO basis (see the relevant part of the output file in the Supplemental Information Section). Such interactions can also account for a smaller bond order than 2, as the calculated Wiberg bond index [29] for the Ge=C bond is 1.6575. Figure 3b,c shows the shape of the lone pair orbital (LP) on the phosphorus and the σ -antibond orbital on the Ge-C atom. Note that the LP bearing orbital matches the phase of σ -antibond (red coloured in Figure 3c), and this interaction is enhanced by the bending of the PCGe skeleton.

Figure 3. Lone-pair- σ^* hyperconjugation in the case of the P=C=Ge unit (a) between the P lone pair (b) and the σ^* orbital on the Ge-C bond (c) in the case of HP=C=GeH₂

Another significant interaction with the same effect in the decrease of the Ge-C bond order is a charge transfer from a P-H bonding orbital to the π -symmetry antibond orbital on the Ge-C bond (Figure 4a).

Figure 4. σ - π^* interaction (a) between the P-H bond orbital (b) and the Ge-C antibonding NB orbital (c) in the model phosphagermaallene HP=C=GeH₂

The effect that different substituents containing group 13 to 17 elements on the germanium atom would have on the bond order of the Ge-C bond in phosphagermaallenes has been investigated by B3LYP/6-311G(d, p) calculations on the model compounds shown in Table 5.

Table 5. B3LYP/6-311G(d,p) geometrical data and Wiberg bond indexes for model phosphagermaallenes

Molecule	HP=C=Ge(BH ₂)H	HP=C=Ge(BH ₂) ₂	HP=C=Ge(CH ₃)H	HP=C=Ge(CH ₃) ₂
Ge-C (pm)	180.1	182.5	177.9	177.9
C-P (pm)	163.5	163.6	164.1	164.2
P-C-Ge (°)	170.8	171.9	160.7	160.5
Ge-C bond order	1.52	1.43	1.62	1.57
Molecule	HP=C=Ge(SiH ₃)H	HP=C=Ge(SiH ₃) ₂	HP=C=Ge(NH ₂)H	HP=C=Ge(NH ₂) ₂
Ge-C (pm)	178.5	178.9	179.6	179.7
C-P (pm)	164.0	164.2	164.7	164.3
P-C-Ge (°)	163.5	166.1	147.0	155.9
Ge-C bond order	1.64	1.64	1.50	1.40
Molecule	HP=C=Ge(OMe)H	HP=C=Ge(OMe) ₂	HP=C=GeFH	HP=C=GeF ₂
Ge-C (pm)	163.8	182.9	179.0	185.9
C-P (pm)	178.1	164.7	168.3	164.3
P-C-Ge (°)	167.0	147.6	162.7	147.1
Ge-C bond order	1.51	1.36	1.52	1.34

The largest bond order is calculated for substituents containing group 14 elements, like CH₃ and SiH₃. The calculation was also carried out for a phosphagermaallene bearing a SiMe₃ group on the germanium atom to check if the Si-H bond is not the one determining the higher bond order through stabilizing hyperconjugation effects towards the Ge=C unit, and also because SiH₃ would make a poor experimental choice. The results for HP=C=Ge(SiMe₃)₂ were similar to those obtained for HP=C=Ge(SH₃)₂ with a calculated Wiberg bond order of 1.6396. The most

important interaction that leads to the decrease in the Ge=C bond strength remains the donation of electron density from the P lone pair to the antibond orbital oriented on the Ge-C bond.

The low bond order in the case of the model compound HP=C=GeF₂ is explained by supplementary interactions due to the presence of the fluorine atom, bearing electron lone pairs (Figure 5).

Figure 5. Non-bonding orbitals involved in hyperconjugation leading to Ge=C destabilization in HP=C=GeF₂ (a) lone pair on F, b) π^* orbital on the Ge-C bond)

The NBO analysis shows a strong delocalization the lone pair oriented perpendicular to the Ge-F bond to the π^* orbital on the Ge-C bond and both fluorine atoms display this type of interaction. Figure 5 shows the shape of the orbitals involved. The other lone pair is oriented perpendicular to the π^* orbital and cannot contribute to the mentioned hyperconjugative effect.

III. Outlook

The Ge=C bond in phosphagermaallenes is weakened by a hyperconjugative effect directed from the P lone pair to the Ge-C bonding orbital. Substituents with atoms bearing lone pairs or vacant *p* orbitals induce other types of charge transfer which also result in the weakening of the Ge=C bond order, while groups containing group 14 elements like Si and C are found to be “inert” and such substituents might stabilize the PCGe skeleton, still leaving access to the functionality of the double bonds.

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Supplementary information on the MP4 and CCSD optimized geometries, geometrical data relative energies and results on the second order perturbation NBO analysis is available at or on the request from the authors.

References:

1. A. G. Brook, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. K. Kallury, *J. Chem. Soc., Chem. Commun.*, 191, (1981).
2. J. Escudié, H. Ranaivonjatovo, and L. Rigon, *Chem. Rev.*, **100**, 3639 (2000).
3. J. Escudié, H. Ranaivonjatovo, M. Bouslikhane, Y. El Harouch, L. Baiget, G. Cretiu Nemes, *Russ. Chem. Bull.*, **53**, 1020 (2004).
4. J. Escudié, H. Ranaivonjatovo, *Organometallics*, **26**, 1542 (2007).
5. M. A. Chaubon, B. Dittrich, J. Escudie, H. Ramdane, H. Ranaivonjatovo, J. Satge, *Synth. React. Inorg. Met-Org. Chem.*, **27**, 519 (1997).
6. G. Nemes, J. Escudie, I. Silaghi-Dumitrescu, H. Ranaivonjatovo, L. Silaghi-Dumitrescu, H. Gornitzka, *Organometallics*, **26**, 5136 (2007).
7. P. M. Petrar, G. Nemes, I. Silaghi-Dumitrescu, H. Ranaivonjatovo, H. Gornitzka, J. Escudié, *Chem. Commun.*, **40**, 4149 (2007).
8. H. Ramdane, H. Ranaivonjatovo, J. Escudié, S. Mathieu, and N. Knouzzi, *Organometallics*, **15**, 3070 (1996).
9. Y. El Harouch, H. Gornitzka, H. Ranaivonjatovo, J. Escudié, *J. Organomet. Chem.*, **643-644**, 202 (2002).
10. A.D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993).
11. C. Lee, W. Yang, and R.G. Parr, *Phys. Rev. B*, **37**, 785 (1988).
12. S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.*, **58**, 1200 (1980).
13. P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, *J. Phys. Chem.*, **98**, 11623 (1994).
14. Wavefunction Inc. 18401 Von Karman Avenue, Suite 370 Irvine, CA 92612.
15. H. Basch, *Inorg. Chim. Acta*, **252**, 265 (1996).
16. C.L. Chin-Hung Lai, M. Su, and S. Y. Chu, *J. Phys. Chem. A*, **106**, 575 (2002).
17. A. H. Cowley, S. W. Hall, C. M. Nunn, and J. M. Power, *Chem. Commun.*, 753 (1988).
18. Z. Rappoport, editor, *The Chemistry of Organic Germanium, Tin and Lead Compounds*, 2 vols., (John Wiley & Sons, 2002).
19. J. Cizek, *Adv. Chem. Phys.*, **14**, 35 (1969).
20. G. D. Purvis and R. J. Bartlett, *J. Chem. Phys.*, **76**, 1910 (1982).
21. G. E. Scuseria, C. L. Janssen, and H. F. Schaefer III; *J. Chem. Phys.*, **89**, 7382 (1988).
22. G. E. Scuseria, H. F. Schaefer III, *J. Chem. Phys.*, **90**, 3700 (1989).
23. R. Krishnan, J. A. Pople, *Int. J. Quant. Chem.*, **14**, 91 (1978).
24. *Gaussian 98, Revision A.6*, 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, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.
25. R. Kakkar, R. Garg, P. Chadha, *J. Mol. Struct. (Theochem)*, **617**, 141 (2002).
26. H. L. Woodcock, H. F. Schaefer, and P. R. Schreiner, *J. Phys. Chem. A*, **106**, 11923 (2002).
27. NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold.
28. B. E. Eichler, D. R. Powell, and R. West, *Organometallics*, **17**, 2147 (1998).
29. K.B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

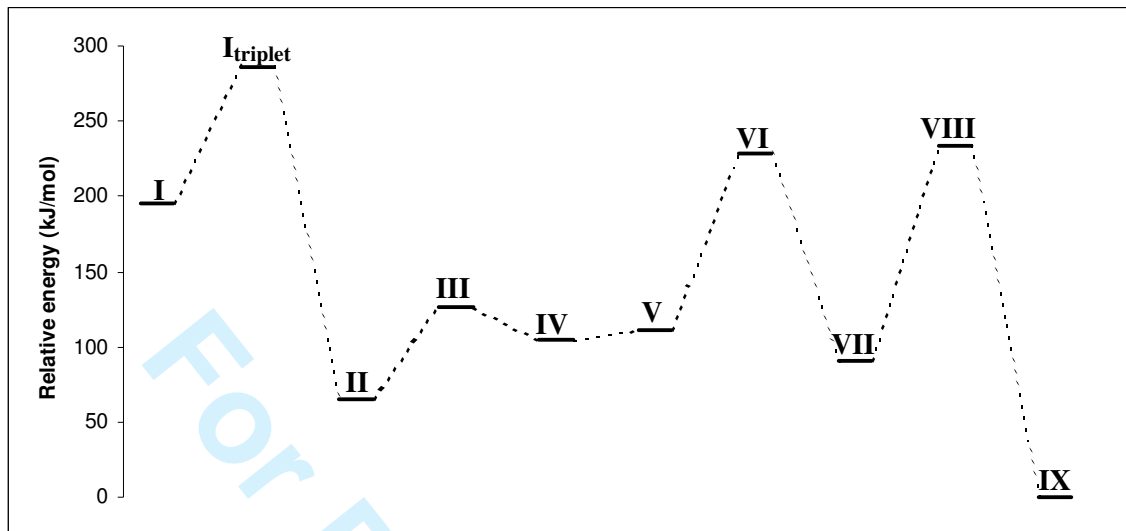


Figure 1. Relative energies in kJ/mol (compared to the series minimum IX) of CH_3GeP isomers

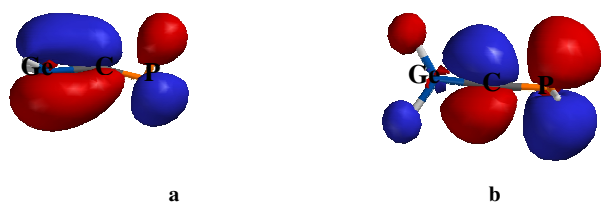
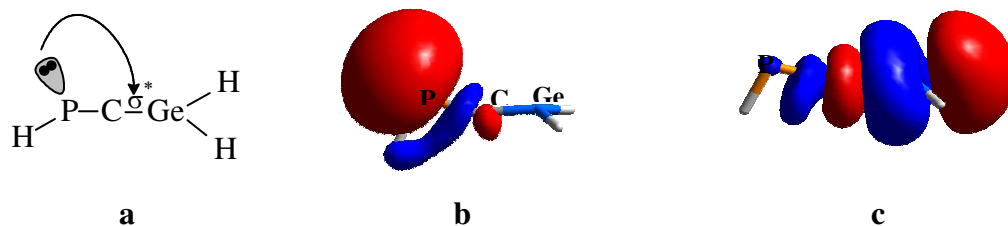
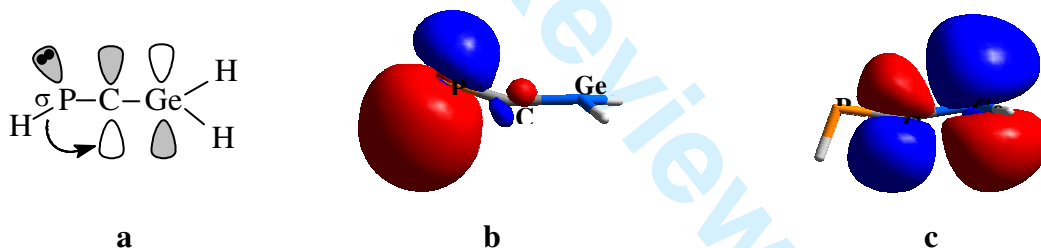


Figure 2. HOMO (a) and LUMO (b) orbitals of $\text{HP}=\text{C}=\text{GeH}_2$ I



15 **Figure 3.** Lone-pair- σ^* hyperconjugation in the case of the P=C=Ge unit (**a**) between the P lone pair (**b**)
16 and the σ^* orbital on the Ge-C bond (**c**) in the case of HP=C=GeH₂



41 **Figure 4.** σ - π^* interaction (**a**) between the P-H bond orbital (**b**) and the Ge-C antibonding NB orbital (**c**) in
42 the model phosphagermaallene HP=C=GeH₂

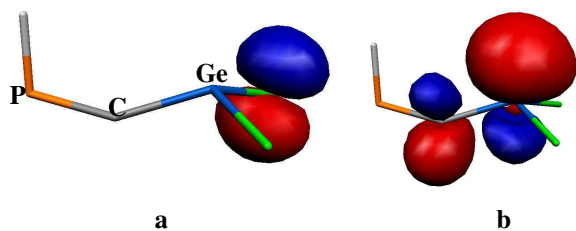


Figure 5. Non-bonding orbitals involved in hyperconjugation leading to Ge=C destabilization in HP=C=GeF₂ (a) lone pair on F, (b) π^* orbital on the Ge-C bond

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An Insight into the Structure of Model Germaphosphaallenes

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Supplementary information:

Table S1. Calculated CCSD/6-31G(d,p) energies and geometrical parameters for HP=C=GeH₂ isomers

Table S2. Calculated MP4(SDQ)/6-31G(d,p) energies and geometrical parameters for HP=C=GeH₂ isomers

Figure S1. Variation of the relative energies calculated with CCSD/6-31G(d, p) and MP4/6-31G(d, p) for isomers **I-IX**

Table S4. Calculated B3LYP/6-31G(d,p) energies for isomers **I-IX**

Table S5. Calculated B3LYP/6-31G(d,p) energies for isomers **I-Me-IX-Me**

Table S6. Excerpt from the second order perturbation theory analysis of Fock Matrix in NBO basis for (a) HP=C=GeH₂ and (b)HP=C=GeF₂

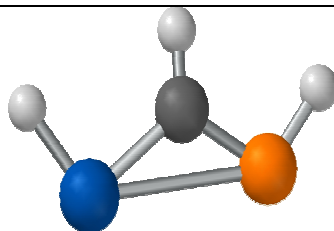
¹ Corresponding author. Email : isi@chem.ubbcluj.ro

Table S1. Calculated CCSD/6-31G(d,p) energies and geometrical parameters for HP=C=GeH₂ isomers

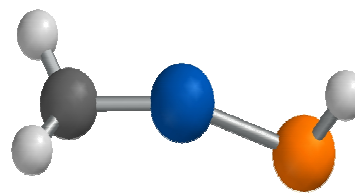
Molecule	I	I_{triplet}
Total Energy (a.u.)	-2453.839071	-2453.725295
ΔE (kJ/mol)	203.05	502.21
Ge-C (pm)	178.4	175.8
P-C (pm)	164.8	164.8
Ge-C-P ($^{\circ}$)	164.04	163.97

Molecule	II	III
Total Energy (a.u.)	-2453.898196	-2453.869169
ΔE (kJ/mol)	47.60	123.94
Ge-C (pm)	191.7	194.1
P-C (pm)	155.6	197.2
Ge-C-P ($^{\circ}$)	179.84	65.30

Molecule



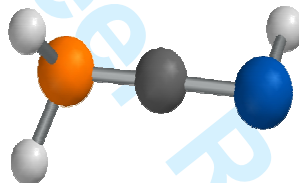
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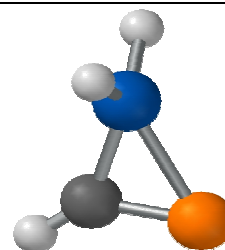
V

Total Energy (a.u.)	-2453.867485	-2453.869561
ΔE (kJ/mol)	126.12	122.89
Ge-C (pm)	197.2	179.2
P-Ge (pm)	310.5	214.0
P-Ge-C ($^\circ$)	29.23	157.82

Molecule



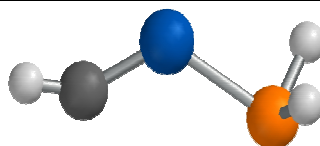
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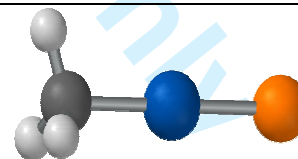
VII

Total Energy (a.u.)	-2453.811658	-2453.884057
ΔE (kJ/mol)	275.16	84.76
Ge-C (pm)	177.8	191.5
P-C (pm)	171.7	168.6
Ge-C-P ($^\circ$)	170.35	79.87

Molecule



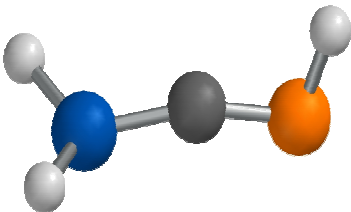
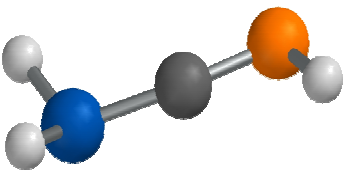
VIII

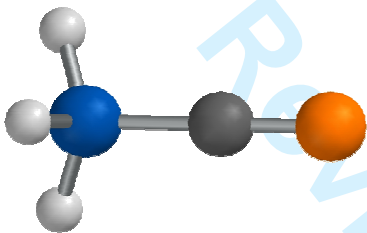
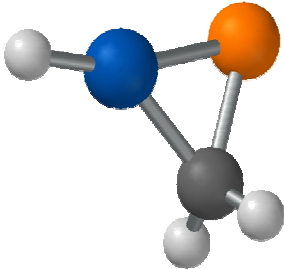


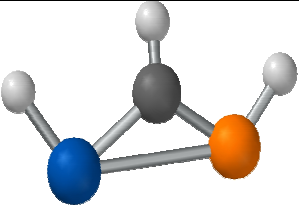
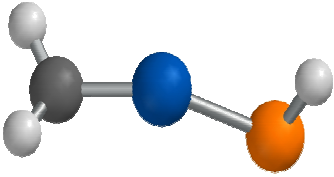
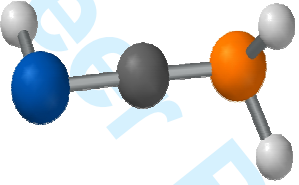
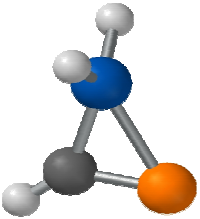
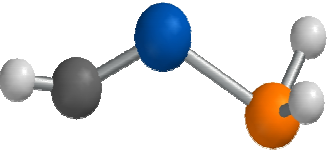
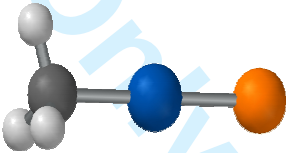
IX

Total Energy (a.u.)	-2453.823081	-2453.91631
ΔE (kJ/mol)	245.12	0.00
Ge-C (pm)	172.3	195.3
P-Ge (pm)	232.8	202.8
P-Ge-C ($^\circ$)	129.16	179.92

Table S2. Calculated MP4(SDQ)/6-31G(d,p) energies and geometrical parameters for HP=C=GeH₂ isomers

Molecule		
	I	I_{triplet}
Total Energy (a.u.)	-2453.838522	-2453.724823
ΔE (kJ/mol)	204.22	503.18
Ge-C (pm)	178.9	179.0
P-C (pm)	165.0	164.5
Ge-C-P (°)	162.56	160.05

Molecule		
	II	III
Total Energy (a.u.)	-2453.898768	-2453.867939
ΔE (kJ/mol)	45.80	126.87
Ge-C (pm)	191.8	195.3
P-C (pm)	156.0	198.7
Ge-C-P (°)	179.82	58.28

Molecule		
	IV	V
Total Energy (a.u.)	-2453.866262	-2453.868517
ΔE (kJ/mol)	131.27	125.36
Ge-C (pm)	197.1	179.2
P-Ge (pm)	309.9	213.6
P-Ge-C ($^\circ$)	29.40	156.79
Molecule		
	VI	VII
Total Energy (a.u.)	-2453.808344	-2453.88359
ΔE (kJ/mol)	283.58	85.73
Ge-C (pm)	180.1	191.3
P-C (pm)	1.666	168.7
Ge-C-P ($^\circ$)	177.84	79.82
Molecule		
	VIII	IX
Total Energy (a.u.)	-2453.819879	-2453.916201
ΔE (kJ/mol)	253.24	0.00
Ge-C (pm)	172.3	195.3
P-Ge (pm)	231.6	203.1
P-Ge-C ($^\circ$)	136.31	179.91

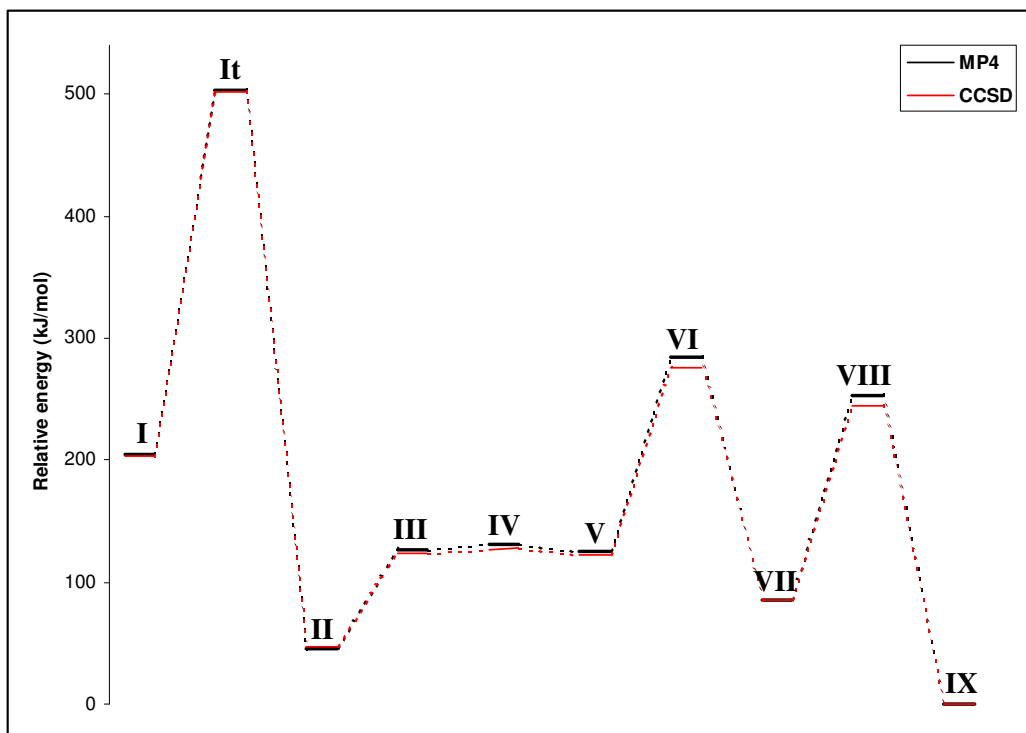


Figure S1. Variation of the relative energies calculated with CCSD/6-31G(d, p) and MP4/6-31G(d, p) for isomers **I-IX**

Table S4. Calculated B3LYP/6-31G(d,p) energies for isomers **I-IX**

Molecule	Total energy (a.u.)
I	-2457.92568
It	-2457.891415
II	-2457.97514
III	-2457.951919
IV	-2457.960168
V	-2457.957917
VI	-2457.913166
VII	-2457.965443
VIII	-2457.911001
IX	-2458.000005

Table S5. Calculated B3LYP/6-31G(d,p) energies for isomers I-Me-IX-Me

Molecule	Total energy (a.u.)
I-Me	-2575.906811
I _r -Me	-2575.871256
II-Me	-2575.95922
III-Me	-2575.917116
IV-Me	-2575.930853
V-Me	-2575.91525
VI-Me	-2575.892586
VII-Me	-2575.94575
VIII-Me	-2575.887026
IX-Me	-2575.947134

Table S6. Excerpt from the second order perturbation theory analysis of Fock Matrix in NBO basis for (a) HP=C=GeH₂ and (b)HP=C=GeF₂

(a)

<i>Donor NBO (i)</i>	<i>Acceptor NBO (j)</i>	<i>E(2)</i> <i>kcal/mol</i>	<i>E(j)-E(i)</i> <i>a.u.</i>	<i>F(i,j)</i> <i>a.u.</i>
1. BD(1)P1-H2	/104. BD*(2) C3 -Ge4	7.74	0.40	0.050
28. LP(1)P1	/103. BD*(1) C3-Ge4	10.22	0.76	0.079

(b)

<i>Donor NBO (i)</i>	<i>Acceptor NBO (j)</i>	<i>E(2)</i> <i>kcal/mol</i>	<i>E(j)-E(i)</i> <i>a.u.</i>	<i>F(i,j)</i> <i>a.u.</i>
30. LP(1)P3	/124. BD*(1)Ge1- C2	13.08	0.72	0.088
33. LP(3)F5	/125. BD*(2)Ge1- C2	9.83	0.30	0.051
36. LP(3)F6	/125. BD*(2)Ge 1- C2	9.83	0.30	0.051