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The Relative Stabilities of 1,3-Diphospha-2-silaallene and Some of Its Isomers

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An ab initio investigation of the relative stability of 1,3-diphospha-2-silaallenes (RP=Si=PR) with respect to potential isomers shows that the allene isomer is not the global minimum throughout a series of several substituents (R = H, SiH_3, CH_3, Ph, F) – the siladiphosphirene isomer is significantly more stable for all these substituents. The stability of the diphosphasilaallene relative to other isomers depends on the nature of the adjacent substituents. Thus, for simple carbon and silyl substituents alternative ring-closed isomers are favored over the diphosphasilaallene, which, depending on the substituent, can show silylene or phosphasilene character. The results obtained at the DFT level are compared with those at other levels of theory for the parent system.

Introduction

Numerous investigations dealing with the stabilization and bonding situation of multiply bonded phosphorus and silicon compounds have initiated a fertile research area. Multiple bonds between silicon and phosphorus are synthetically especially challenging due to the high reactivity of such unsaturated systems. Nevertheless, sterically protected Si=P double bonds have been generated and structurally characterized.[1–5] Similarly, phosphaallenes[6–15] as well as silaallenes,[16–19] trisilaallenes,[20–22] and even a 1-phospha-3-silaallene[23] have been synthesized and studied theoretically,[24–30] although the combination of both heteroatoms directly bonded to each other within a single allene system remains unknown so far. Earlier attempts to generate 1,3-diphospha-2-silaallenes by hydrogen chloride abstraction from suitable precursors with sterically hindered bases resulted either in Si–P bond cleavage or addition of the base to the Si–P unit.[31,32] The availability of seemingly suitable precursors of the type $(RPH)_2SiCl_2$ combined with a lack of information concerning the outcome of attempted synthesis of 1,3-diphospha-2-silaallenes prompted us to investigate their stability with respect to possible isomers theoretically. According to our findings, the 1,3-diphospha-2-silaallene structure, despite being a local minimum, is not the global minimum on the potential energy hypersurface. For all substituents considered in our investigation the cyclic siladiphosphirene is by far the most stable isomer. Which isomer is the next most stable one depends significantly on the nature of the adjacent substituent. However, in neither case was the silaallene the second most stable isomer. For systems bearing carbon substituents we find that a cyclic phosphasilene isomer is more stable than the silaallene, while for more electropositive substituents a cyclic diphosphasilylene structure is lower in energy. As our results show, the relative stability of the isomers explored by us strongly depends on the electronic properties of the adjacent substituents.

Results and Discussion

In order to investigate the energetic separation of 1,3-diphospha-2-silaallene and its isomers, we performed ab initio quantum chemical calculations using the program package Gaussian 03,[33] employing a 6-311G(d) basis set[34–37] at the Hartree–Fock and DFT(B3LYP) level.[38,39] The harmonic vibrational frequencies and their infrared intensities for all of the optimized structures were evaluated by the B3LYP method. Complete reports of the vibrational frequencies and infrared intensities are given in the Supporting Information. These results were used to determine if a structure is a genuine minimum. The final energy values include zero-point correction and thermal correction to 298 K. The reliability of the B3LYP method for the calculation of the structures and the stability of the group of compounds under investigation was tested by the higher correlated MP2 method for the hydrogen-substituted parent systems of all isomers.

For our calculations we considered the diphosphasilaallene structure **1**, the cyclic diphosphasilylene structures with the adjacent substituents adopting a *cis* and a *trans* position (**2** and **3**), the ring-opened diphosphenyl silylene structure **4**, the cyclic phosphasilene **5**, siladiphosphirene **6**, and finally phosphasilyne **7** (Scheme 1). Other isomers such as the vinylidene silylene **8** or phosphanylidenes like **9** were not taken into account since exploratory calculations on the parent system at the B3LYP//6-311G(d) level showed that

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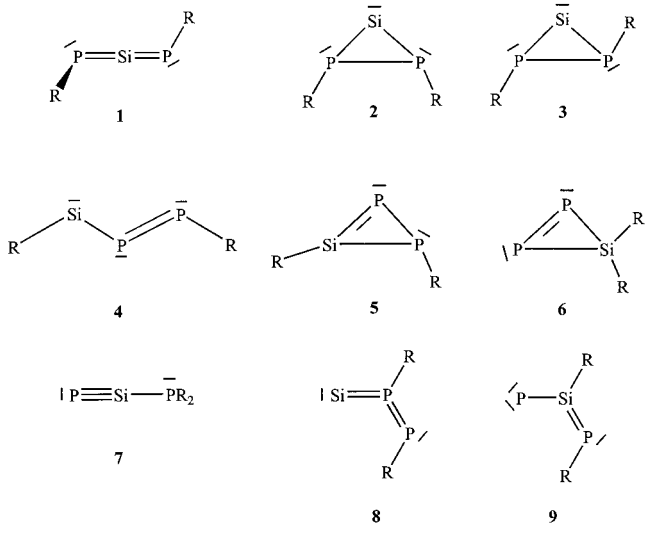
they are roughly 20 kcal mol^{-1} higher in energy than the least stable of the other isomers. To explore the electronic influence of different substituents on the relative energies of these isomers, we investigated the hydrogen-substituted parent systems **1**–**7a**, the silyl derivatives **1**–**7b**, the methyl derivatives **1**–**7c**, the phenyl derivatives **1**–**7d**, and the fluorine-substituted derivatives **1**–**7e**. Since we were mainly interested in exploring the effect of the electronic properties of different substituents on the stability of the 1,3-diphospha-2-silaallene, we focused our attention only on its monomeric isomers. Nevertheless, it is obvious that in the case of insufficient steric protection dimers or oligomers of these isomers will be even lower in energy. Although it appears worthwhile to investigate this aspect, it exceeds the scope of this investigation, which is mainly aimed at the possibility of predicting the electronic influence of the substituents in order to realize the unsaturated isomers discussed herein synthetically.



Scheme 1. Idealized structures of isomers of 1,3-disphospha-2-silaallenes (R = H, SiH_3, CH_3, Ph, F).

The relative energies obtained for the differently substituted isomers **1**–**7** are summarized in Table 1. As is evident from these data, the 1,3-diphospha-2-silaallene is not the global minimum on the energy hypersurface. Nevertheless, the diphosphasilaallene structure is a local minimum for all these substituents.

For all substituents considered in our investigation (R = H, SiH_3, CH_3, Ph, F) the siladiphosphirene structure **6** is the most stable isomer. The relative stability of this isomer is most pronounced for the fluorine-substituted **6e** and lowest for the silyl-substituted **6b**. The geometric parameters of this isomer show a related trend (Table 2). As expected, the P=P bond in most examples of isomer **6** shows values typical for a double bond and the Si–P distance is typical for the corresponding single bond. Interestingly, these bonds show a counteracting trend for **6e** and **6b**. Thus, the P=P bond in **6b** (2.056 Å) is the shortest observed in this series while the corresponding Si–P bond is the longest (2.250 Å). The opposite is observed for the highly electronegative fluorine substituted **6e**, which shows the longest P=P bond in this series (2.124 Å) along with the shortest Si–P bond (2.160 Å). In fact for the fluorine derivative, both of these values are right in the middle between typical single and double bonds of these elements. Concomitant with this trend of the bond lengths, the angles associated with the substituents also show related effects. For fluorine as substituent the R–Si–R angle (ca. 105°) is the smallest in this series, while for silyl substituents this angle is the largest (ca. 118°).

Table 2. Geometrical parameters for the structural isomer **6**.

	P–P [Å]	Si–P [Å]	P–P–Si [°]	R–S–P [°]	P–Si–P [°]	R–Si–R [°]
R = H (**6a**)	2.069	2.220	62.28	119.19	55.58	113.09
R = SiH_3 (**6b**)	2.056	2.250	62.91	117.27	54.25	117.99
R = CH_3 (**6c**)	2.079	2.220	62.14	119.70	55.71	111.82
R = Ph (**6d**)	2.078	2.220	62.24	119.70	55.72	113.20
R = F (**6e**)	2.124	2.160	60.56	122.03	58.88	104.94

These findings can be rationalized based on the considerations that have been developed for phosphirenes. where the phosphirene ring is considered as the combination of a (hetero)carbene and a triple bond.[40,41] Similarly, the diphosphirene could be considered as the combination of a silylene and P≡P. The stronger the interaction of these fragments, the higher should be the P–Si bond order and hence the shorter this bond length. In contrast, the P–P bond order should be reduced by increasing interaction of P_2 with the silylene fragment and the P–P bond length should therefore increase. Consequently, the main effect of the substituents in **6** would be to affect the electronic nature of the silylene fragment and hence the extent of its interaction with the P_2 fragment. It is well known that fluoro-substituted silylenes possess a singlet ground state that is more favorable to interact with a P_2 unit, while the triplet ground state is stabilized by silyl substituents. The strong interaction between these fragments in **6e** should also be increased

Table 1. Relative energies [kcal mol^{-1}] for isomers **1**–**7** including ZPE and thermal energy correction for 298.2 K computed at the B3LYP//6-311g(d) level. TS = one imaginary frequency.

	1	**2**	**3**	**4**	**5**	**6**	**7**
R = H (**a**)	24.53	16.67	16.13	36.07	24.06	0.00	25.09
R = SiH_3 (**b**)	14.98	9.56	7.42	33.70	18.17	0.00	19.07
R = CH_3 (**c**)	44.60	32.77	31.77	77.31 (TS)	27.54	0.00	36.63
R = Ph (**d**)	39.08	27.26	24.97	33.48	23.95	0.00	36.60
R = F (**e**)	92.28	83.65 (TS)	79.43 (TS)	46.79	49.24	0.00	75.41

by additional negative hyperconjugation,[42,43] where σ*(Si-F) states act as acceptors towards bonding π(P≡P) states.

Apart from the most stable siladiphosphirene **6**, the nature of the next stable isomer depends significantly on the properties of the adjacent substituent. For the hydrogen- and silyl-substituted species the cyclic diphosphasilylene structure **3** carrying the substituents in a *trans* orientation is the second most stable isomer. Structure **3** is around 8 kcal mol^{-1} more stable than the 1,3-disphospha-2-silaallene structure **1**. For all substituents the *cis* isomer **2a**–**e** is only around 1–4 kcal mol^{-1} less stable than the *trans* isomers **3a**–**e**, thus indicating only a minor repulsive interaction between the substituents. On changing the substituents to methyl or phenyl a somewhat different picture is obtained. In these cases the phosphasilene structure **5**, to which some partial silyl cation character might be attributed, is the second most stable isomer rather than the diphosphasilylene structure **3**. The energy difference between these two isomers is not large (1–4 kcal mol^{-1}), however.

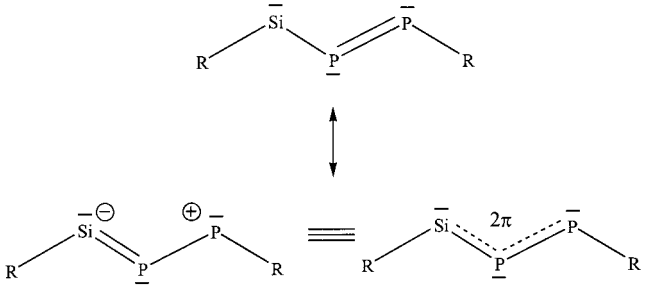
The relative stability of isomers **3** and **5** can be rationalized by taking the charge distribution within the PPSi system into account. On the grounds of Mulliken charges calculated for the phosphorus and silicon atoms within isomers **3** and **5** it is obvious that for hydrogen- and silyl-substituted derivatives the charge distribution differs substantially from the carbon- and fluorine-substituted derivatives. Of the isomers under question those with the more negative (less positive) charge at the more electronegative phosphorus atoms represents the energetically more favored structure (Table 3). Consequently for R = CH_3, Ph, and F the phosphasilene isomer **5** is more stable, while the cyclic *trans* isomer **3** is favored for R = H and SiH_3.

Table 3. Sums of Mulliken charges for the P and Si atoms in isomers **3** and **5**.

	Phosphasilene **5**		*trans* Ring **3**	
R = H (**a**)	q(Si)	0.207	q(Si)	0.238
	Σq(PP)	–0.271	Σq(PP)	–0.348
R = SiH_3 (**b**)	q(Si)	0.126	q(Si)	0.200
	Σq(PP)	–0.337	Σq(PP)	–0.350
R = CH_3 (**c**)	q(Si)	0.459	q(Si)	0.220
	Σq(PP)	–0.113	Σq(PP)	0.042
R = Ph (**d**)	q(Si)	0.435	q(Si)	0.127
	Σq(PP)	–0.099	Σq(PP)	0.197
R = F (**e**)	q(Si)	0.567	q(Si)	0.221
	Σq(PP)	0.191	Σq(PP)	0.514

For fluorine as substituent the second most stable isomer is the ring-opened structure **4**. The latter is about 2 kcal mol^{-1} more stable than the cyclic phosphasilene **5e** and about 33 kcal mol^{-1} more stable than the *trans* oriented cyclic structure **3e**. Apart from the global minimum **6e**, structures **4e** and **5e** are the only isomers with direct Si–F bonds, therefore their relative stability is likely to be a consequence of the strength of the silicon–fluorine bond. In contrast, structure **4** is about 10–50 kcal mol^{-1} higher in energy than the second most stable isomer for most other substituents (R = H, CH_3, SiH_3). In fact, structure **4a**–**c** is the least stable isomer for these substituents and even a transition state for R = CH_3 which transforms into **5c** and connects the two enantiomeric forms of **5** as we found based on IRC calculations. Interestingly, the phenyl substituent has a somewhat intermediate position and **4d** is only 10 kcal mol^{-1} less stable than **5d**. This indicates that the π-donor properties of fluorine and phenyl stabilize structure **4**.

For structure **4** a delocalized bond situation can be expected. Formally, this could be described as a silylene-substituted diphosphene. However, it is obvious that other resonance forms have to be considered. This isomer is probably best described as a 2π-SiPP allylic system where significant interaction of the substituents with the central unit can be neglected (Scheme 2). However, such a description requires a planar or nearly planar arrangement of the SiPP unit and the adjacent substituents. According to our findings (Table 4), such a situation is realized only in the methyl- and fluoro-substituted derivatives **4c**,**e** and to a lesser extent for phenyl-substituted **4d**. In contrast, the substituents adjacent to the SiPP unit in the hydrogen- and silyl-substituted derivatives **4a**,**b** deviate by almost 90° from the planar geometry. Nevertheless, the geometric parameters in **4b**,**c** show almost equally long Si–P and P–P bond lengths, which differ by 0.08–0.09 Å. The Si–P distances in **4b**,**c** (2.02 and 2.11 Å, respectively) are in a range for P–Si bond lengths that is significantly shorter than a P–Si single bond (2.25 Å).[3,5] In contrast to the σ-acceptor, π-donor substituents fluorine and phenyl, this P–Si bond length increases substantially to 2.31 and 2.35 Å, which is in the range for a single bond. Hydrogen-substituted **4a** shows an intermediate situation, with an Si–P bond length of 2.22 Å. The central Si–P–P angle follows a similar trend (86–90°) and is markedly smaller for fluorine- and phenyl-substituted derivatives **4d**,**e** than for the other substituents (**4a**–**c**: 117–144°).



Scheme 2. Mesomeric Lewis structures of **4**.

The trends observed for the structures of isomers **4a**–**e** (Table 4) can be interpreted as a dominant contribution of the silylene-substituted diphosphene resonance structure. Interaction of π-donor substituents such as phenyl and fluorine can stabilize the adjacent silylene center to an extent that makes this isomer more stable than the cyclic isomer **3**, as in the case of fluorine. Given a nearly planar arrangement, such a stabilized silylene center (as in **4d**,**e**) shows only a low tendency to interact with the neighboring diphosphene unit. For less stabilized and therefore more electrophilic silylene centers such as in **4c**, interaction with the adjacent diphosphene unit is much stronger. In nonplanar

arrangements such as found for **4a**,**b**, an effective Si–P–π interaction is precluded by the geometric situation, which tends to lead to an isolated (i.e. short) P=P bond along with a rather long Si–P bond.

Table 4. Geometric parameters for the structural isomer **4**.

	Si–P–P [°]	Si–P [Å]	P–P [Å]	R–Si–P [°]	P–P–R [°]	RSi···PR [°]
R = H (**4a**)	116.93	2.220	2.040	91.27	94.87	84.80
R = SiH_3 (**4b**)	143.48	2.110	2.030	91.66	97.72	88.94
R = CH_3 (**4c**)	129.75	2.020	2.110	144.22	96.40	0.00
R = Ph (**4d**)	90.00	2.310	2.060	100.41	89.99	10.06
R = F (**4e**)	86.13	2.350	2.020	96.05	105.33	0.00

Isomer **3** can be described as a cyclic diphosphasilylene in which the silylene center can interact with the adjacent phosphorus atoms. The structure of this isomer is almost invariant to the adjacent substituents with respect to the central ring (Table 5). Only for R = F it is not a minimum structure and ring opens to **1**. Generally, the Si–P bond length is about 2.28–2.29 Å, in the typical single bond range for these elements. The P–P bond length varies slightly more and is shortest in fluorine-substituted **3e** (2.12 Å); it is between 2.22 and 2.28 Å for the other substituents. The central P–Si–P angle varies only slightly (55–60°) and is close to experimental values in diphosphasiliranes.[44] Similarly, the P–P–Si angle of the three-membered ring shows values in a narrow range between 60–63°. In contrast to the central ring unit, more significant differences are observed for the angles involving the adjacent substituents, i.e. the R–P–Si and the dihedral angle R–P–P–R. For R–P–Si the angle increases with the π-donor character of R. In contrast, the dihedral angle R–P–P–R decreases in the same direction (Table 5).

Table 5. Geometric parameters for the structural isomer **3**.

	P–Si–P [°]	Si–P [Å]	P–P–Si [°]	R–P–Si [°]	P–P [Å]	R–P–P–R [°]
R = H (**3a**)	58.85	2.290	60.57	92.79	2.259	178.26
R = SiH_3 (**3b**)	59.81	2.280	60.09	87.88	2.283	170.54
R = CH_3 (**3c**)	58.11	2.280	60.76	110.27	2.222	155.72
R = Ph (**3d**)	59.11	2.260	59.25	91.05	2.266	158.22
R = F (**3e**)	55.05	2.290	62.47	121.05	2.123	126.79

The structural parameters for the 1,3-disphospha-2-silaallenes **1a**–**e** also show some interesting trends depending on the nature of the adjacent substituents (Table 6). The deviation from linearity of the central P=Si=P unit [P–Si–P angle of 135° (**1e**) and 155° (**1d**)] is strongest for the π-donating substituents fluorine and phenyl. Concomitant with this bending is an increase of the P–Si bond length to 2.12 (**1e**) and 2.09 Å (**1d**). The corresponding hydrogen- and silyl-substituted analogues (**1a**,**b** 169–171°) are closer to linearity and the P–Si bond (2.06 Å) is shorter than for the phenyl- and fluorine-substituted derivatives (**1e**,**d**).

Table 6. Geometric parameters for the structural isomer **1**.

	P–Si–P [°]	Si–P [Å]	R–P–Si [°]	RP···PR [°]
R = H (**1a**)	168.87	2.060	89.83	88.69
R = SiH_3 (**1b**)	171.36	2.060	93.50	89.14
R = CH_3 (**1c**)	161.98	2.080	102.89	90.58
R = Ph (**1d**)	155.38	2.090	102.17	94.16
R = F (**1e**)	135.46	2.120	104.40	99.34

Among all isomers of 1,3-disphospha-2-silaallene the cyclic phosphasilene **5** shows the least impact of the electronic properties of the substituents on its structural parameters (Table 7). Thus, in **5a**–**e** the formal double bond between the silicon atom and phosphorus atom without any exocyclic substituent shows values in the range of 2.04–2.06 Å. The formal single bond from silicon to the other phosphorus atom is characteristically longer, with values between 2.17 and 2.23 Å that are in agreement with a description as a short single bond. The P–P distances (2.38–2.41 Å) are rather long, and the angles are in a narrow range for all substituents that we investigated. Thus, the P–Si–P angles in **5a**–**e** vary only from 68° to 69° and similarly the P(R)–P–Si angles are all within the range of 58° to 59°.

Table 7. Geometric parameters for the structural isomer **5**.

	Si–P [Å]	Si–P(R) [Å]	P–P [Å]	P–Si–P [°]	P(R)–P–Si [°]	R–Si–P–R [°]
R = H (**5a**)	2.046	2.210	2.410	68.91	58.79	87.74
R = SiH_3 (**5b**)	2.059	2.230	2.390	67.88	59.43	85.76
R = CH_3 (**5c**)	2.051	2.200	2.390	68.38	58.86	84.57
R = Ph (**5d**)	2.057	2.200	2.380	67.95	58.94	77.88
R = F (**5e**)	2.040	2.170	2.380	69.02	58.06	78.60

The cyclic isomers of 1,3-diphospha-2-silaallene (**2**, **3**, **5**, and **6**) are generally not as structurally flexible as the ring-opened isomers **1** and **4**. One might be tempted to interpret this rigidity as an indication of a limited or even negligible interaction between the substituents and the cyclic P_2Si unit. However, the presence and significance of such an interaction is evident from the prominent influence of different substituents on the relative stabilities of these isomers, including the cyclic ones.

Finally, the last isomer investigated by us is the phosphanyl-substituted phosphasilyne **7** (Table 8). Since the substituents in this isomer are not bonded directly to a low-valent main group atom, structural differences based on their conjugative properties are not likely to be pronounced. Accordingly, the formal triple bond shows a constant P–Si distance of roughly 1.97 Å for all substituents. The adjacent Si–P single bond (2.23 Å) is shortest for silyl-substituted **7a** and longest for fluorine-substituted **7e** (2.35 Å). The angles around the tricoordinate phosphorus atom are smallest for the hydrogen-substituted compound and largest for its phenyl-substituted congener, which suggests steric reasons for this observation.

Table 8. Geometric parameters for the structural isomer **7**.

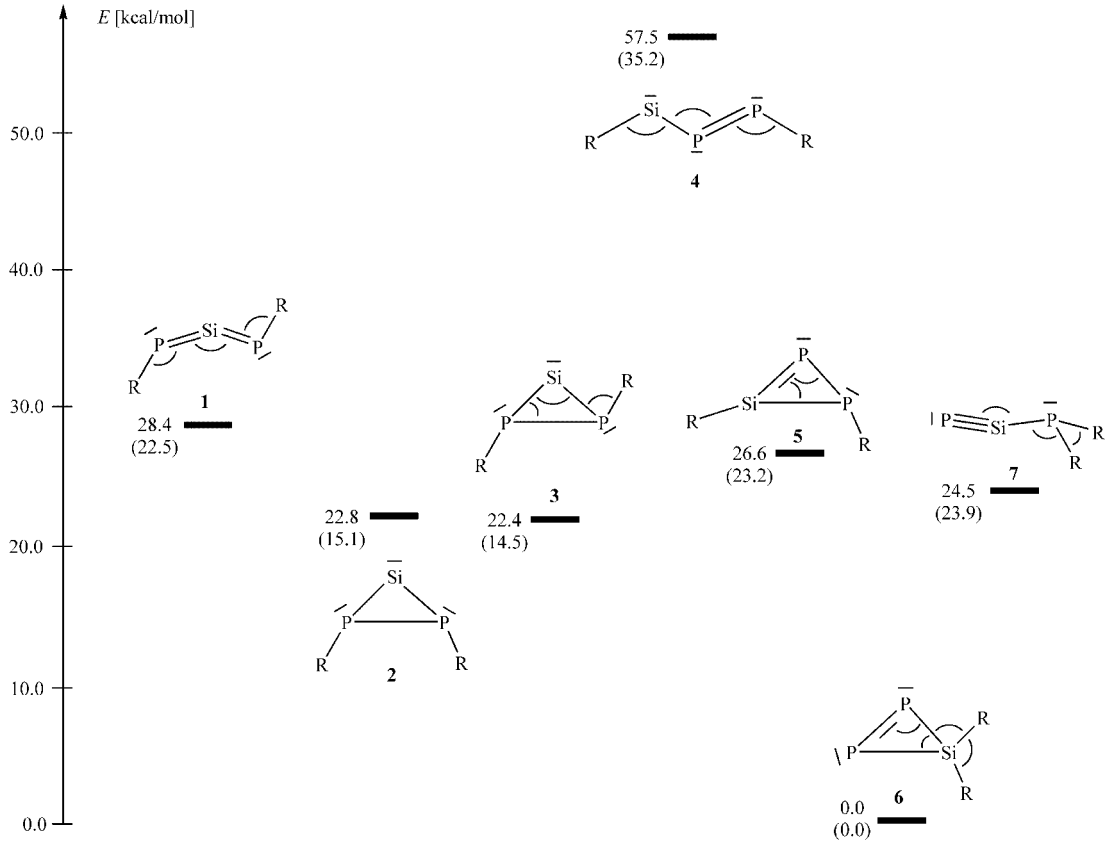
	Si≡P [Å]	Si–PR_2 [Å]	P–Si–P [°]	Si–P–R [°]	R–P–R [°]	P–Si–P–R [°]
R = H (**7a**)	1.966	2.260	170.38	93.95	93.72	132.97
R = SiH_3 (**7b**)	1.968	2.230	175.34	98.23	100.48	128.97
R = CH_3 (**7c**)	1.971	2.270	170.55	100.23	100.57	128.28
R = Ph (**7d**)	1.971	2.270	168.48	100.33	105.20	110.32
R = F (**7e**)	1.976	2.350	154.16	98.81	98.56	129.99

In order to check the reliability of the B3LYP method and the basis set of our choice for the structurally rather flexible compounds investigated here we tested the structure and energy calculations for the hydrogen-substituted parent systems of all isomers by reoptimization using the MP2 method. Table 9 and Scheme 3 summarize the results obtained for isomers **1**–**7a** with the 6-311g(d) and 6-311g(d,p) basis sets using the DFT and MP2 approach to include electron correlation. As is evident from these data, the differences with respect to correlation method and basis set are only marginal and the same trend in the relative energies of isomers **1**–**7a** is observed in all cases, which indicates that the DFT approach is well suited to exploring the energy hypersurface of this type of compounds. A minor issue is observed for isomer **4**, which is the least stable isomer for all methods. Interestingly, structure **4** is identified as a minimum when employing the B3LYP functional while two negative vibrations at low frequency are found at the MP2 level. Bearing in mind that DFT methods are known to sometimes incorrectly predict minima on a very flat energy hypersurface and for spin contaminated states,[45] it might be possible that this isomer could in fact be a transition state in other cases as well. Actually, methyl-substituted **4c** is a TS even at the DFT level and this isomer is generally the least stable one, except for **4d**,**e**. Therefore, for the fluorine-substituted system, where structure **4e** is quite relevant due to its high relative stability, the minimum was confirmed also at the MP2 level.

Table 9. Relative energies [kcal mol^{-1}] for isomers **1**–**7a** (R = H) including ZPE and thermal energy correction for 298.2 K at different levels of theory.

	1	**2**	**3**	**4**	**5**	**6**	**7**
B3LYP//6-311g(d)	24.5	16.7	16.1	36.1	24.1	0.0	25.1
B3LYP//6-311g(d,p)	22.5	15.1	14.5	35.2	23.2	0.0	23.9
MP2//6-311g(d)	32.3	26.1	25.9	59.2	28.0	0.0	26.2
MP2//6-311g(d,p)	28.4	22.8	22.4	57.5	26.6	0.0	24.5

A limitation of our study that should be relevant for the synthetic realization of such systems is the fact that we focused strictly on the electronic properties of the adjacent substituents and did not consider steric effects and the bulk of the substituents. Nevertheless, it is obvious that sterically very demanding substituents will destabilize structures in which both substituents are connected to the same atom, as



Scheme 3. Overview of relative energies [kcal mol^{-1}] for isomers **1**–**7a** (R = H) at the MP2 level (B3LYP in brackets) using a 6-311g(d,p) basis set including ZPE and thermal energy correction for 298.2 K.

in **7** or the global minimum **6**, whereas the other isomers should benefit from such an influence.

In summary, our exploration of the relative stabilities of 1,3-diphospha-2-silaallenes and their isomers shows that the goal to prepare a stable 1,3-diphospha-2-silaallene will be a hard one to achieve as the siladiphosphirene isomer is significantly more stable for all substituents considered in this study. The stability of the diphosphasilaallene relative to other isomers depends strongly on the nature of the adjacent substituents. Thus, for simple carbon and silyl substituents alternative ring-closed isomers are favored over the diphosphasilaallene, which, depending on the substituent, can show silylene or phosphasilene character. Given sufficient steric protection, the latter species themselves will surely be challenging synthetic goals to pursue.

Computational Details

Quantum chemical calculations were carried out using the Gaussian 03 suite of programs.[33] In related work studying the effect of basis sets and electron correlation on several double-bonded silicon species using different basis sets and several correlation methods, it was found that the geometry is not sensitive to the basis set and good results are expected with standard density functional theory methods.[30,46,47]

The optimized geometry was confirmed as a minimum on the potential surface by second-derivative calculations. All the calculated energy data were corrected with the zero-point energy (ZPE) and the thermal energy correction to 298 K ($E = E_0 + E_{vib} + E_{rot} + E_{transl}$).

Supporting Information (see also the footnote on the first page of this article): Complete data of harmonic vibrational frequencies, optimized geometries, total energies (E, in hartrees), and number of imaginary vibrational frequencies are provided for all isomers.

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[1] C. N. Smit, F. M. Look, F. Bickelhaupt, *Tetrahedron Lett.* **1984**, *25*, 3011.
[2] C. N. Smit, F. Bickelhaupt, *Organometallics* **1987**, *6*, 1156.
[3] E. Niecke, E. Klein, M. Nieger, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 751.
[4] M. Driess, S. Rell, H. Pritzkow, *J. Chem. Soc., Chem. Commun.* **1995**, 253.
[5] D. Lange, E. Klein, H. Bender, E. Niecke, M. Nieger, R. Pietschnig, W. W. Schoeller, H. Ranaivonjatovo, *Organometallics* **1998**, *17*, 2425.
[6] R. Appel, P. Fölling, B. Josten, M. Siray, V. Winkhaus, F. Knoch, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 619.
[7] H. H. Karsch, H. U. Reisacher, G. Mueller, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 618.
[8] R. Appel, V. Winkhaus, F. Knoch, *Chem. Ber.* **1986**, *119*, 2466.
[9] G. Märkl, U. Herold, *Tetrahedron Lett.* **1988**, *29*, 2935.
[10] G. Märkl, S. Reithinger, *Tetrahedron Lett.* **1988**, *29*, 463.
[11] G. Märkl, P. Kreitmeier, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1360.
[12] M. Yoshifuji, K. Toyota, T. Niitsu, N. Inamoto, Y. Okamoto, R. Aburatani, *J. Chem. Soc., Chem. Commun.* **1986**, 1550.
[13] M. Yoshifuji, S. Sasaki, N. Inamoto, *Tetrahedron Lett.* **1989**, *30*, 839.
[14] M. Yoshifuji, S. Sasaki, N. Inamoto, *J. Chem. Soc., Chem. Commun.* **1989**, 1732.
[15] M. Yoshifuji, T. Niitsu, D. Shiomi, N. Inamoto, *Tetrahedron Lett.* **1989**, *30*, 5433.
[16] G. E. Miracle, J. L. Ball, D. R. Powell, R. West, *J. Am. Chem. Soc.* **1993**, *115*, 11598.
[17] M. Trommer, G. E. Miracle, B. E. Eichler, D. R. Powell, R. West, *Organometallics* **1997**, *16*, 5737.
[18] B. Eichler, R. West, in *Advances in Organometallic Chemistry*, vol. 46, **2001**, pp. 1.
[19] B. E. Eichler, G. E. Miracle, D. R. Powell, R. West, *Main Group Met. Chem.* **1999**, *22*, 147.
[20] S. Ishida, T. Iwamoto, C. Kabuto, M. Kira, *Nature* **2003**, *421*, 725.
[21] T. Iwamoto, T. Abe, C. Kabuto, M. Kira, *Chem. Commun.* **2005**, 5190.
[22] T. Iwamoto, H. Masuda, C. Kabuto, M. Kira, *Organometallics* **2005**, *24*, 197.
[23] L. Rigon, H. Ranaivonjatovo, J. Escudie, A. Dubourg, J. P. Declercq, *Chem. Eur. J.* **1999**, *5*, 774.
[24] D. J. Berger, P. P. Gaspar, R. S. Grev, F. Mathey, *Organometallics* **1994**, *13*, 640.
[25] M. S. Gordon, R. D. Koob, *J. Am. Chem. Soc.* **1981**, *103*, 2939.
[26] G. Maier, H. Pacl, H. P. Reisenauer, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1439.
[27] J. C. Barthelat, G. Trinquier, G. Bertrand, *J. Am. Chem. Soc.* **1979**, *101*, 3785.
[28] M. H. Lien, A. C. Hopkinson, *Chem. Phys. Lett.* **1981**, *80*, 114.
[29] M. T. Nguyen, H. Vansweevelt, L. G. Vanquickenborne, *Chem. Ber.* **1992**, *125*, 923.
[30] T. Veszprémi, K. Petrov, C. T. Nguyen, *Organometallics* **2006**, *25*, 1480.
[31] K. Hassler, F. Mitter, B. Reiter, *J. Organomet. Chem.* **1989**, *376*, C1.
[32] E. Niecke, E. Klein, personal communication.
[33] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. Montgomery, J. A., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, Revision C.02 ed., Gaussian, Inc., Wallingford CT, **2004**.
[34] K. Raghavachari, J. A. Pople, E. S. Replogle, M. Head-Gordon, *J. Phys. Chem.* **1990**, *94*, 5579.
[35] M. J. S. Dewar, C. H. Reynolds, *J. Comput. Chem.* **1986**, *7*, 140.
[36] A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639.
[37] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650.
[38] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
[39] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
[40] F. Mathey, *Chem. Rev.* **1990**, *90*, 997.
[41] D. Gonbeau, G. Pfister-Guillouzo, *Nouv. J. Chim.* **1985**, *9*, 71.
[42] A. J. Kos, P. v. R. Schleyer, *Tetrahedron* **1983**, *39*, 1141.

[43] A. E. Reed, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1990**, *112*, 1434.
[44] M. Weidenbruch, M. Herrndorf, A. Schäfer, *J. Organomet. Chem.* **1985**, *295*, 7.
[45] C. J. Cramer, *Essentials of Computational Chemistry*, John Wiley & Sons, New York, **2004**.
[46] T. Veszprémi, M. Takahashi, J. Ogasawara, K. Sakamoto, M. Kira, *J. Am. Chem. Soc.* **1998**, *120*, 2408.
[47] T. Veszprémi, M. Takahashi, B. Hajgató, M. Kira, *J. Am. Chem. Soc.* **2001**, *123*, 6629.

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