DOI: 10.1002/ejic.200700782

Theoretical Design of Silicon–Phosphorus Triple Bonds: A Density Functional Study

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Keywords: Triple bonds / Phosphorus / Silicon / Density functional calculations

A density functional study on the effects of bulky aryl substituents on silicon–phosphorus triple bonds was carried out by using the B3LYP/3-21G* method. These investigations suggest that both the kinetic and thermodynamic stabilities of substituted (L–Si≡P–L)$^{+1}$ molecules are strongly dependent on the substituents (L). That is to say, the triply bonded (L–Si≡P–L)$^{+1}$ molecule can be synthetically accessible by a proper choice of bulky aryl substituents.

Introduction

In the past three decades, chemical bonding between silicon and a heteroatom has received considerable attention because of its importance in inorganic, organic, and physical chemistry.[1] In particular, interest in silicon–phosphorus chemistry has grown tremendously in recent years. The reason for this is twofold. Firstly, the detection of the species SiP in the interstellar/circumstellar gas is now a possibility worth exploring, since these are cosmically abundant species (P/H = 3×10^{-7}, Si/H = 3×10^{-5}).[2] Secondly, SiP bonding is relevant to the manufacture of electronic devices.[3] For instance, phosphorus-doped silicon is one of the principal n-type materials used for MOS gates in semiconductors.[4] Also, it has been reported that, when phosphorus dopants are added in small quantities, significant effects on growth rates are observed. For example, small quantities of PH_3 can lead to a decrease by a factor of 20 in the polysilicon growth rate.[5] As a result, understanding the chemical bonding in silicon–phosphorus compounds can help us construct detailed chemical kinetic models for the interaction of silicon–phosphorus species in the gas phase during the thermal deposition of doped silicon from silane and phosphane.

Compounds with Si–P single bonds and Si=P double bonds have been studied extensively from both experimental and theoretical viewpoints by many groups. Interested readers can find excellent articles in refs.[6–9] It was commonly accepted that compounds having multiple bonds between heavier main group elements bearing bulky substituents would be able to exist as stable species.[10] In fact, as mentioned above, many compounds having a double bond between silicon and phosphorus have been isolated as stable compounds by taking advantage of kinetic stabilization with appropriately bulky substituents as steric protection groups.[11–13] This makes it possible to characterize these compounds spectroscopically and to study their reactivity. Nevertheless, far less is known about Si≡P triple bonds. In contrast to the wealth of experimental information on the Si=P double-bond molecules, no similar direct detection of a –Si≡P– triply bonded compound has been reported so far. A possible explanation for the nonexistence of such triply bonded compounds is the difference in electronegativity [x(P) – x(Si) = 0.3].[14] This may cause the silicon–phosphorus π-system to be rather polarized, readily leading to dimerization or polymerization. As a consequence, the synthesis of stable triple-bond compounds containing silicon and phosphorus will be a particular challenge to synthetic chemists.

Likewise, there are currently only very few theoretical studies on compounds containing Si≡P triple bonds. Early calculations by Gordon and co-workers examined the SiP species as a prototype of the triple bond.[15] Furthermore, according to the density functional theory (DFT) computational results of Lai, Su, and Chu, highly electronegative substitution at silicon can greatly stabilize the triply bonded XSi≡P species relative to the double bonded Si=PX isomer.[16] However, none of the studies have dealt with the existence and relative stabilities of such –Si≡P– triply bonded molecules.

One may thus wonder whether the –Si≡P– triply bonded molecules, in which the silicon and phosphorus atoms both have one attached ligand, can be synthetically accessible and isolable as stable molecules. To accomplish this, one should choose substituents that perform more than one function. Firstly, both substituents must be large enough to protect the silicon–phosphorus triple bond from reactions (such as dimerization). Secondly, since such silicon–phosphorus triply bonded molecules contain a positive charge,

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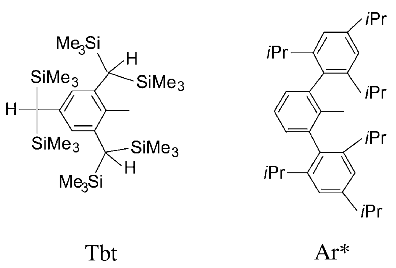
the substituents must protect this charge from attack by other nucleophilic groups (such as halide ions). Thirdly, both substituents must be inert towards the external attacking reagents. In the present work, we have chosen substituents that fulfill all of the above criteria. As far as we are aware, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt, **1**)[17] and 2,6-bis(2,4,6-triisopropylphenyl)phenyl (Ar*, **2**),[18] which are shown in Scheme 1, are known as representative large substituents that are useful for the synthesis and stabilization of multiply bonded species. We therefore chose them as potential protecting groups that are able to stabilize the –Si≡P– triply bonded molecule.



Scheme 1.

Here, we report the first DFT (B3LYP/3-21G*) study of the triply bonded compounds $(L–Si≡P–L)^{+1}$ in the anticipation that such theoretical information will be useful for further experimental considerations. That is, we shall use the computational results to predict that molecules containing a $(L–Si≡P–L)^{+1}$ triple bond with bulky substituents (L) can be thermodynamically stable and are separated by significant barriers from their corresponding isomers (vide infra), perhaps making such $(L–Si≡P–L)^{+1}$ species synthetically accessible.

It should be pointed out here that our study using the B3LYP/3-21G* method to explore the stabilization of the triply bonded $(L–Si≡P–L)^{+1}$ system does not imply that other larger computational effects requiring more comprehensive methods or basis sets are not important. It only means that we acknowledge that the size of the systems currently studied prevents highly accurate optimizations in the quantum theoretical calculations. In particular, their cost and the computational facilities that they require make them impractical. We thus chose to treat such species at the B3LYP/3-21G* level of theory. Highly accurate relative energies between the stationary points can be considered later, the results of which may or may not affect the intramolecular isomerization reactions studied here. In view of recent dramatic developments in silicon and phosphorus chemistry,[19,11e] it is therefore hoped that our theoretical study will provide a crucial starting point for developing silicon and phosphorus triply bonded molecules and for opening up new synthetic areas.

Theoretical Methods

All geometries were fully optimized without imposing any symmetry constraints, although in some instances the resulting structure showed various elements of symmetry. The sequential conformation analyses for each stationary point was first performed by using the Hartree–Fock calculations (RHF/3-21G*). Thus, the model compounds $(L–Si≡P–L)^{+1}$ (L = Tbt, **1**; L = Ar*, **2**) have 988 (638 electrons) and 882 (558 electrons) basis functions, respectively. Vibrational frequency calculations at the RHF/3-21G* level were used to characterize all the stationary points as either minima (no imaginary frequencies) or transition states (one imaginary frequency). It is well-known that the Hartree–Fock level of theory is insufficient for even a qualitative description of the chemical potential energy surface. Thus, these stationary points were then further calculated at the B3LYP/3-21G* level by using the opt = readfc keyword with a tight convergence option (maximum gradient convergence tolerance = 5.0×10^{-5} hartree/bohr). Due to the limitation of both CPU time and memory size available,[20] the B3LYP zero-point energy (ZPE) could not be applied for all of the $(L–Si≡P–L)^{+1}$ systems in the present work. That is, because frequencies were not calculated for all of the species at the B3LYP/3-21G* level of theory, ZPE corrections were performed by using the RHF/3-21G* data. Nevertheless, the addition of these corrections does not change our conclusions. All the calculations were performed with the GAUSSIAN 03 package of programs.[21]

Results and Discussion

In this section, we first discuss the structures of the reactants [i.e., $(L–Si≡P–L)^{+1}$]. The selected geometrical parameters for these stationary points calculated at the B3LYP/3-21G* level are collected in Figure 1. Cartesian coordinates for these stationary points are included in the Supporting Information.

According to our Hartree–Fock frequency calculations, the two reactants have no imaginary frequency and represent true minima on the potential energy surfaces. The global energy-minimum structures, $(Tbt–Si≡P–Tbt)^{+1}$ and $(Ar^*–Si≡P–Ar^*)^{+1}$, are predicted with a silicon–phosphorus triple-bond length of 2.066 and 2.043 Å, respectively, at the B3LYP/3-21G* level of theory (see Figure 1). These values are shorter than the experimental values for the Si–P single bond (2.254 Å)[6c] and of the Si=P double bond (2.094 Å).[16] Previous theoretical studies, however, pointed out that the bond length of the Si≡P triple bond in the L–Si≡P molecule is predicted to be in the range 1.956–1.987 Å at the B3LYP/6-311++G** level of theory.[16] This indicates that further improvement of the basis set beyond 3-21G* should have a significant influence on the predicted Si≡P interatomic distance. Although it would be desirable to carry out this and even higher-level calculations, we were constrained by the available CPU time and disk space. Nevertheless, the focus of this study is the structures and potential well depth of all the stationary points, which

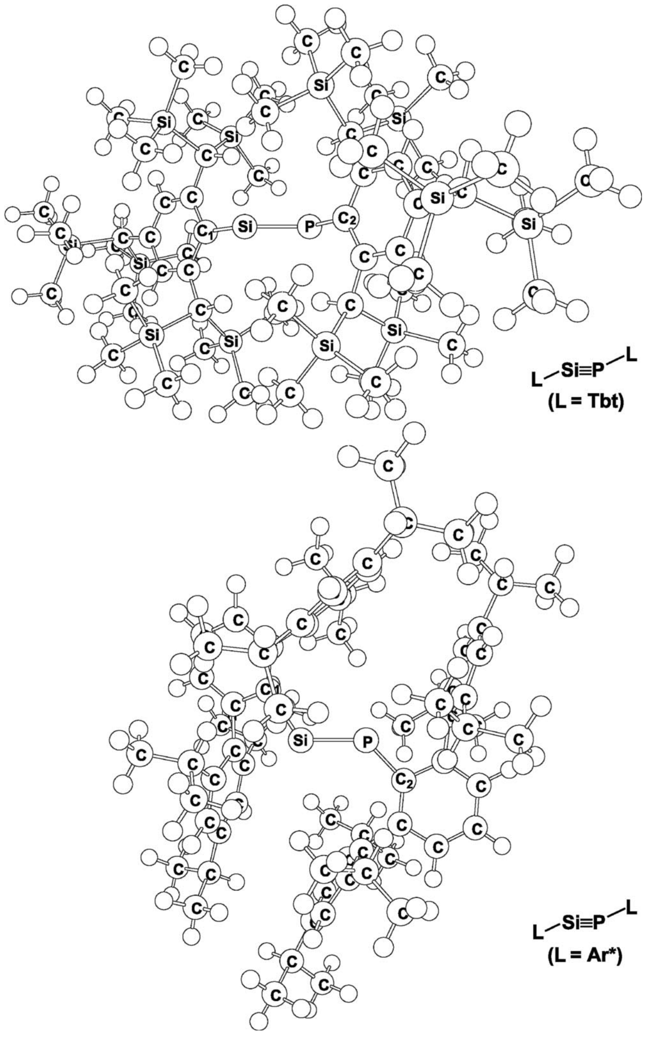
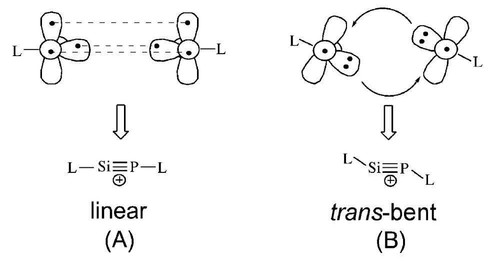


Figure 1. Top: optimized structures of $(\text{Tbt–Si}{\equiv}\text{P–Tbt})^{+1}$ at the B3LYP/3-21G* level of theory. Selected bond lengths [Å]: Si–P 2.072, C^1–Si 1.819, P–C^2 1.796. Selected bond angles [°]: C^1–Si–P 136.8, Si–P–C^2 123.8, C^1–Si–P–C^2 178.9. Bottom: optimized structures of $(\text{Ar*–Si}{\equiv}\text{P–Ar*})^{+1}$ at the B3LYP/3-21G* level of theory. Selected bond lengths [Å]: Si–P 2.066, C^1–Si 1.856, P–C^2 1.826. Selected bond angles [°]: C^1–Si–P 122.0, Si–P–C^2 130.6, C^1–Si–P–C^2 169.3.

should be more reliable than the geometrical parameters studied in this work. On the basis of such considerations, we continue to use the B3LYP/3-21G* method to analyze the systems studied in the present work.

As can be seen in Figure 1, the triple-bond species preferentially takes up a *trans*-bent structure rather than a linear one. The reason for this may be the phenomenon of orbital nonhybridization.[22,23] Namely, both silicon and phosphorus atoms are reluctant to take part in hybridization.[19,11e] In other words, silicon and phosphorus show a strong tendency to keep the $3s^23p^13p^1$ and $3s^23p^13p^13p^1$ valence electronic configurations without significant hybridization.[10a] As a result, two electrons are singlet-paired in an orbital having a high degree of 3s atomic character, while the other valence electrons are in singly occupied 3p atomic orbitals. Both silicon and phosphorus therefore tend to form a nonbonding orbital of mainly s character, while the remaining p electrons are used up to form bonds with neighboring atoms. Furthermore, one may divide $(\text{L–Si}{\equiv}\text{P–L})^{+1}$ into two parts and analyze the electronic levels of each part.[10a] That is, one may view $(\text{L–Si}{\equiv}\text{P–L})^{+1}$ as being composed of two units, Si–L and $(\text{P–L})^{+1}$ (both with the same number of valence electrons). Consequently, there are two kinds of valence–electron interaction models, as given in Scheme 2. In model (A), the two fragments, Si–L and $(\text{P–L})^{+1}$, are in quartet states ($^4\Sigma$). This produces a linear reactant molecule. In model (B), the two doublet states ($^2\Pi$) of Si–L and $(\text{P–L})^{+1}$ combine to yield the *trans*-bent reactant compound. Then, we fully optimized the structures of these two species at the B3LYP/3-21G* level of theory. Our theoretical calculations demonstrate that the Si–Tbt and Si–Ar* units both have doublet ground states, which are lower than their corresponding quartet states by 50.6 and 54.5 kcal/mol, respectively. Also, $(\text{P–Tbt})^{+1}$ and $(\text{P–Ar*})^{+1}$ are predicted to lie 20.9 and 18.8 kcal/mol (B3LYP/3-21G*) lower than their corresponding quartet state, respectively. Again, all these results strongly support the fact that the Si–L and $(\text{P–L})^{+1}$ units can both be considered as doublet states, in which two electrons occupy the orbital with 3s atomic character, as the orbital nonhybridization[22] model predicted earlier. For these reasons, one can see that model (B) is preferable over model (A) for explaining the *trans*-bent structure of the $(\text{L–Si}{\equiv}\text{P–L})^{+1}$ triply bonded system.[23]



Scheme 2.

In addition to this, the doublet–quartet energy splitting in both Si–L and $(\text{P–L})^{+1}$ species is strongly correlated with the stability of the triply bonded $(\text{L–Si}{\equiv}\text{P–L})^{+1}$ molecule itself. According to the configuration mixing (CM) model based on the theory of Pross and Shaik,[24,25] the smaller the energy gap, ΔE_{dq} ($\Delta E_{\text{dq}} = E_{\text{quartet}} - E_{\text{doublet}}$), between the doublet and the quartet states of the Si–L or $(\text{P–L})^{+1}$ units, the greater the stability of the triply bonded $(\text{L–Si}{\equiv}\text{P–L})^{+1}$ system. Accordingly, the results of our model, shown in Scheme 2, are in agreement with the CM model predictions. That is, the smaller the doublet–quartet energy splitting, ΔE_{dq}, the more favorable the interaction model (B) and, in turn, the easier the formation of a *trans*-bent structure in the triply bonded product.

Furthermore, as a result of the single-fold coordination on both silicon and phosphorus atoms, the presence in $(\text{L–Si}{\equiv}\text{P–L})^{+1}$ of very bulky alkyl substituents may result in the conversion of the triple-bond species into a divalent double-bond species [see Equation (1)] by a shift of one of the two L groups. This leads to the 1,2-shift products, i.e., (:Si=PL$_2$)$^{+1}$ and (L$_2$Si=P:)$^{+1}$, respectively. We have undertaken theoretical calculations (B3LYP/3-21G*) to study the effect of the bulky substituents, L, on the relative stability of (L–Si≡P–L)$^{+1}$, (:Si=PL$_2$)$^{+1}$, and (L$_2$Si=P:)$^{+1}$ isomers and on the transition states connecting them. The intramolecular reaction mechanism is represented as follows: (:Si=PL$_2$)$^{+1}$ → TS–P → (L–Si≡P–L)$^{+}$ (reactant) → TS–Si → (L$_2$Si=P:)$^{+1}$. The potential energy profiles for such 1,2-shift reactions of (L–Si≡P–L)$^{+1}$ (L = Tbt, **1**; L = Ar*, **2**) are collected in Figure 2. Also, their relative energies at the B3LYP level of theory are summarized in Table 1. The geometrical structures of the transition states (TS–P and TS–Si) and the corresponding products [(:Si=PL$_2$)$^{+1}$ and (L$_2$Si=P:)$^{+1}$] are given in Figures 3, 4, 5, and 6. Cartesian coordinates for these stationary points are included in the Supporting Information.

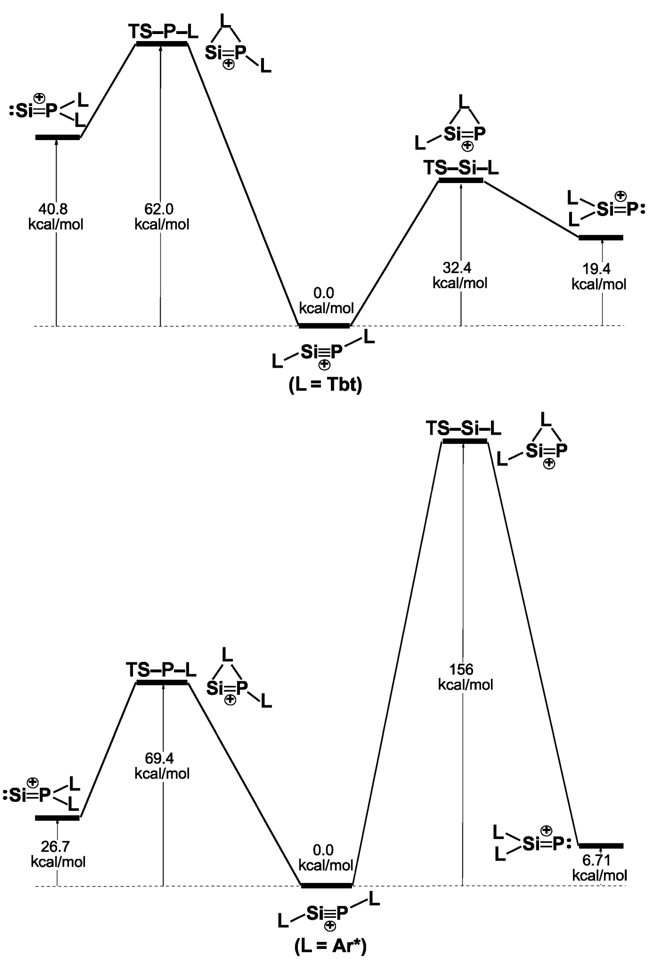
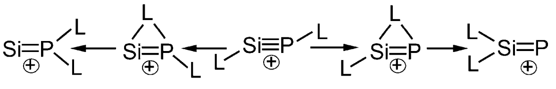


Figure 2. Relative energies, in kcal/mol, of the pathways for the isomerization of the singlet (L–Si≡P–L)$^{+1}$ species. The theoretical method used is at the B3LYP/3-21G* level of theory.

Table 1. Calculated relative energies in kcal/mol for isomers of (L–Si≡P–L)$^{+1}$ (reactant) at the B3LYP/3-21G* level of theory.

Species[a]	(:Si=PL$_2$)$^{+1}$	TS–P–L	(L–Si≡P–L)$^{+1}$	TS–Si–L	(L$_2$Si=P:)$^{+1}$
L = Tbt (**1**)	40.83	62.01	0.0	32.39	19.41
L = Ar* (**2**)	26.86	69.40	0.0	156.3	6.703

[a] For more details, see the text and the Supporting Information.



(L = Tbt, **1**; L = Ar*, **2**) (1)

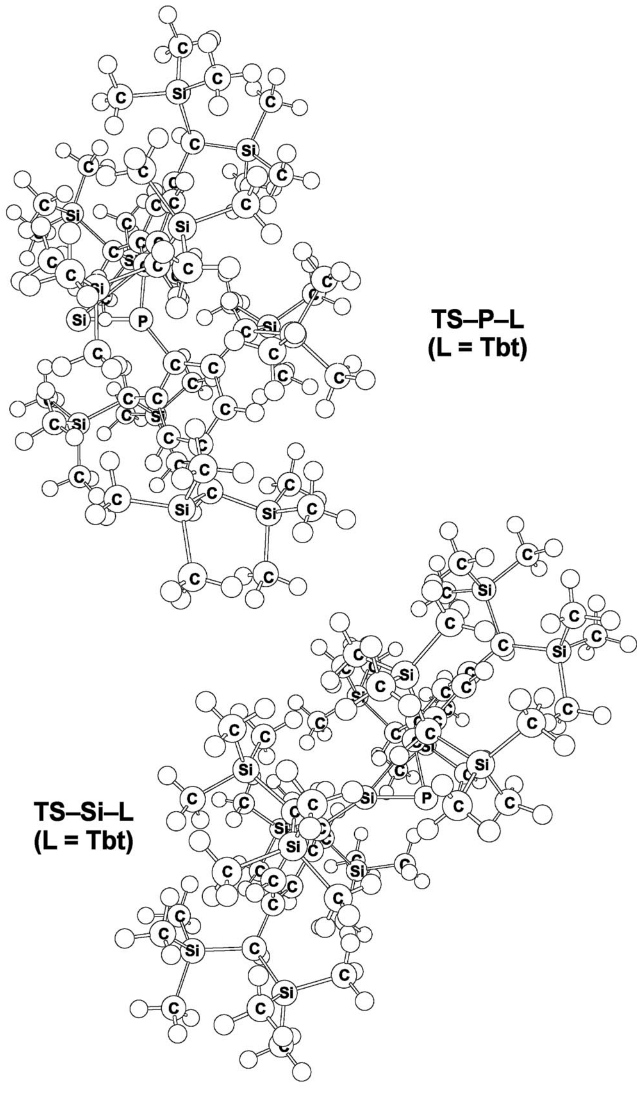


Figure 3. Optimized structures of TS–P–Tbt and TS–Si–Tbt at the B3LYP/3-21G* level of theory. Hydrogen atoms are omitted for clarity. See the text.

From Table 1 and Figure 2, the activation barriers of (Tbt–Si≡P–Tbt)$^{+1}$ are estimated to be 62.0 (TS–Si–Tbt) and 32.4 (TS–P–Tbt) kcal/mol, while those for (Ar*–Si≡P–Ar*)$^{+1}$ are calculated to be 69.4 (TS–Si–Ar*) and 156 (TS–P–Ar*) kcal/mol, respectively, at the B3LYP level of theory. In particular, the DFT calculations showed that the relative energies of isomerization products [(:Si=PL$_2$)$^{+1}$ and (L$_2$Si=P:)$^{+1}$, where L is Tbt or Ar*) are all above those of the corresponding reactants as seen in Figure 2.[26]

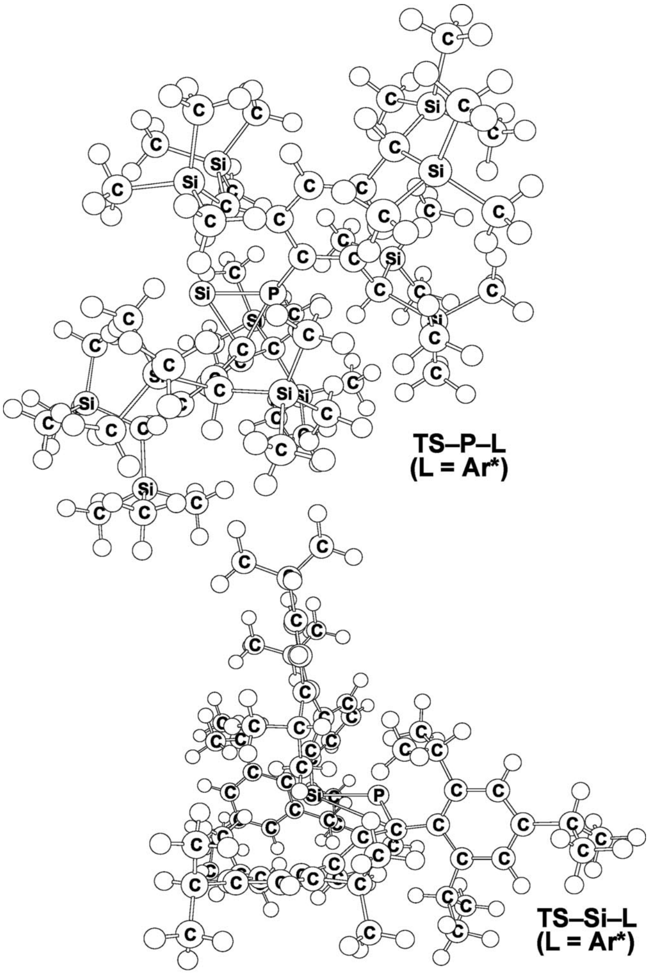


Figure 4. Optimized structures of TS–P–Ar* and TS–Si–Ar* at the B3LYP/3-21G* level of theory. Hydrogen atoms are omitted for clarity. See the text.

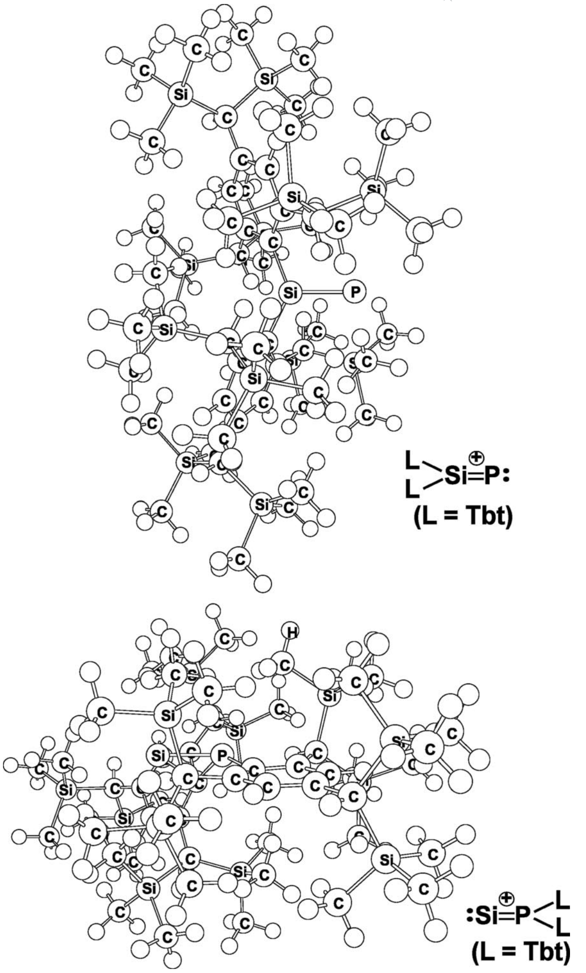


Figure 5. Optimized structures of isomerization products at the B3LYP/3-21G* level of theory. See the text.

The atomic charges for silicon or phosphorus atoms are listed in Table 2. First, this may affect the possibility of dimerization, although this reaction may be prevented by the bulky substituent. Second, since the charge is not localized on Si≡P but on the substituents, a counterion will not easily attack the Si≡P center to destroy the triple bond despite the attachment of bulky substituents.[27]

Table 2. Calculated atomic charges of $(L–Si≡P–L)^{+1}$ (reactant) at the B3LYP/3-21G* level of theory.[a]

Atom	$(:Si=PL_2)^{+1}$	TS–P–L	$(L–Si≡P–L)^{+1}$	TS–Si–L	$(L_2Si=P:)^{+1}$
			L = Tbt (**1**)		
P	0.3244	0.4730	0.09506	0.6550	–0.1521
Si	0.4097	0.2681	0.5195	0.1090	0.8438
			L = Ar* (**2**)		
P	0.3564	0.2992	0.1518	0.3223	0.05042
Si	0.5469	0.5387	0.7349	0.6012	0.8550

[a] For more details, see the text and the Supporting Information.

Thus our work strongly suggests that both triply bonded molecules are kinetically stable with respect to 1,2-migrations, which lead to the production of divalent species. As a consequence, if $(Tbt–Si≡P–Tbt)^{+1}$ and $(Ar^*–Si≡P–Ar^*)^{+1}$ were to be formed directly by the appropriate gas-phase reactions, they should not interconvert easily. The reason for this is presumably attributed to the steric protection effect of the bulky substituent groups (i.e., Tbt and Ar*). Indeed, such doubly bonded species involving divalent silicon or phosphorus atoms are considered to be quite unstable because of steric crowding of both substituents on the same atom, making the divalent atom vulnerable to attack by other reagents. Besides, the large dipole moments of both $(Tbt–Si≡P–Tbt)^{+1}$ (2.71 D) and $(Ar^*–Si≡P–Ar^*)^{+1}$ (3.01 D) at the same level of theory indicate that they should be experimentally observable.[28] Accordingly, one may then predict that the triply bonded molecules, L–Si≡P–L, can be synthetically accessible by use of appropriately bulky substituents.[29]

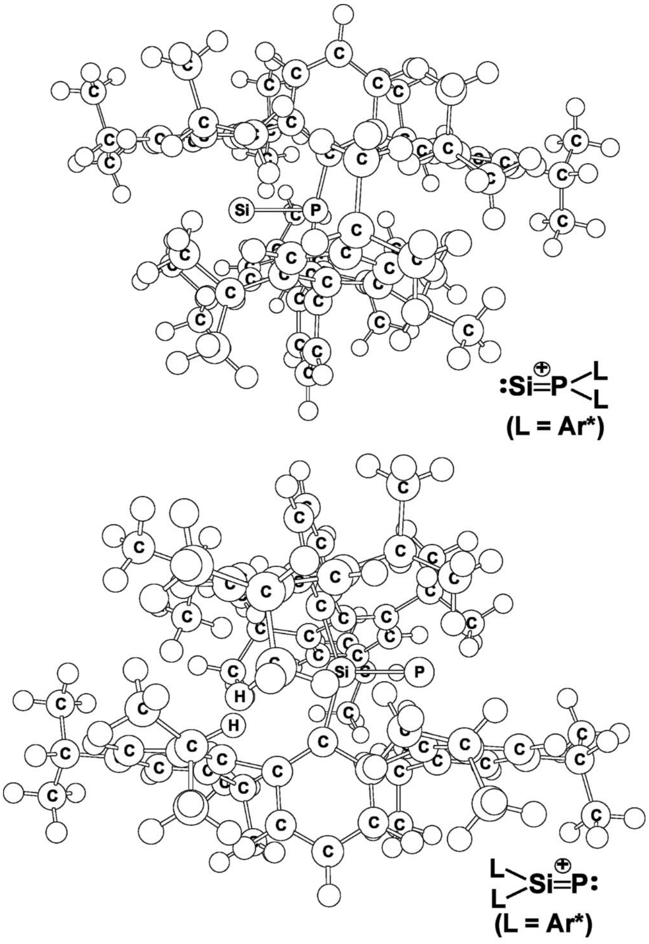


Figure 6. Optimized structures of isomerization products at the B3LYP/3-21G* level of theory. See the text.

Conclusion

In summary, our theoretical work demonstrates that the triply bonded molecule, $(\mathrm{L{-}Si{\equiv}P{-}L})^{+1}$, lies at a minimum on the potential energy surface and can be stabilized and synthesized in both a kinetic and a thermodynamic sense given a proper choice of bulky aryl substituents. We encourage experimentalists to carry out further experiments to confirm our predictions.

Supporting Information (see footnote on the first page of this article): Details of the optimized atomic coordinates and energies of the compounds studied in this work.

Acknowledgments

The authors are grateful to the National Center for High-Performance Computing of Taiwan for generous amounts of computing time. They also thank the National Science Council of Taiwan for the financial support. Special thanks are also due to the referees for very helpful suggestions and comments.

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[26] As suggested by referees, we also calculated the simple molecule (H–Si≡P–H)$^{+1}$ at the B3LYP/3-21G* level theory. Our theoretical findings indicate that the relative energies of (H–Si≡P–H)$^{+1}$ are predicted to be lower than those of (:Si=PH$_2$)$^{+1}$ and (H$_2$Si=P:)$^{+1}$ by 2.9 and 5.1 kcal/mol, respectively. In comparison to the results for (Tbt–Si≡P–Tbt)$^{+1}$ and (Ar*–Si≡P–Ar*)$^{+1}$ shown in Table 1, we estimate the steric effects due to the substituents Tbt and Ar* to be about 1.2 and 38 kcal/mol, respectively.

[27] We thank one of the referees for this comment.

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[29] According to our present calculations (B3LYP/3-21G*), the Si≡P triple-bond lengths for (Tbt–Si≡P–Tbt)$^{+1}$ and (Ar*–Si≡P–Ar*)$^{+1}$ are estimated to be 2.071 and 2.066 Å, respectively. These are in reasonably good agreement with the results of Pyykkö and co-workers. See: a) P. Pyykkö, Y. Zhao, *Mol. Phys.* **1990**, *70*, 701; b) P. Pyykkö, S. Riedel, M. Patzschke, *Chem. Eur. J.* **2005**, *11*, 3511.

Received: July 24, 2007
Published Online: January 15, 2008