Structures, Energetics, and Transition States of the Silicon–Phosphorus Compounds Si$_2$PH$_n$ ($n = 7, 5, 3, 1$). An ab Initio Molecular Orbital Study

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This study examines a variety of compounds containing silicon–phosphorus multiple bonds as well as a selection of hydrogen-bridged species, including a doubly bridged structure. The structures of 29 minima and 37 transition states of the form Si$_3$PH$_n$ ($n = 7, 5, 3, 1$) have been optimized at the MP2(full)/6-31G(d) level of theory; a representative subset was also optimized at the QCISD/6-311G(d,p) level. Relative energies were computed using a modification of the G2 level of theory. The stability of these compounds was investigated with respect to both unimolecular rearrangement and H$_2$ addition/elimination. Barrier heights for 1−2 and 1−3 H-shifts and for H$_2$ addition/elimination span wide ranges and are dependent on the nature of the bonding. Structures that contain true silicon–phosphorus double bonds are particularly stable with respect to unimolecular rearrangement.

Introduction

Interest in silicon–phosphorus chemistry has grown significantly in recent years. Nevertheless, much less is known experimentally about the structure and reactivity of Si−P bonds than other aspects of silicon chemistry. A number of interesting Si−P analogues of hydrocarbon structures have been prepared, including cyclobutane, bicyclobutane, spiropentane, hexane, norbornane, adamantane, and cubane. Compounds with Si=P double bonds are very reactive and can dimerize readily. However, with bulky substituents, Si=P double bonded species can be stabilized sufficiently to permit spectroscopic characterization and X-ray crystal structure analysis. A computational study of the isomerization and unimolecular decomposition of Si=P−H systems would directly aid our understanding of Si−P compounds in inorganic chemistry.

Questions of silicon−phosphorus bonding also arise in the manufacture of electronic devices. Phosphorus-doped silicon is one of the principal n-type materials used for MOS gates in semiconductors. It can be formed by diffusion of dopants into the solid or by in situ doping using chemical vapor deposition (CVD) with a mixture of silane and phosphine. However, some difficulties arise because phosphine tends to passivate the surface even at low concentrations, resulting in a reduction of the deposition rate. This effect is much less severe when disilane is used as the silicon source. It has been suggested by Ahmed et al. that this is due to the stronger adsorption of disilane to the surface. An alternative explanation is that silylene, produced along with silane in the decomposition of disilane, can adsorb to the surface with a sticking probability competitive with that of phosphine. In the gas phase, silylene can easily insert into a phosphine PH bond, with a computed barrier height of less than 2 kcal/mol. The product of this reaction, sillyphosphine, has been observed experimentally in the pyrolysis of a phosphine/disilane mixture. Thus the present theoretical study on Si−P bonding and reactivity could also contribute to our understanding of the gas-phase reactions in the CVD of phosphorus-doped silicon.

Early calculations by Gordon and co-workers examined SiPH$_3$, SiPH$_2$, and SiPH as prototypes of single, double, and triple SiP bonds. Cowley and collaborators studied various isomers of SiPH$_3$ to explore the stability of Si=P double bonds. Schleyer and Kost calculated the bond energy of H$_2$Si=P=PH in a comparison of double-bond energies of second-row elements with carbon and silicon. Raghavachari et al. investigated the insertion of silylene into various species, including PH$_3$. Mains et al. examined the 1,1-elimination of H$_2$ from H$_2$SiPH$_2$ to form HSi=P=H. A number of authors have calculated ring strain energies of heterosubstituted cyclopolsilanes and have noted that cyclic SiH$_2$SiH$_3$PH and other monosubstituted three-membered polysilane rings have unusually short Si−Si bonds. Nyulaszi et al. have calculated HSiPH$_3$ and H$_2$SiPH in connection with a study of substituent effects on the stability of silylenes and silyl radicals. Schoeller and Busch have computed the cations, radicals and anions of H$_2$SiP and SiPH$_2$. Hrušák et al. have also examined cations and radicals in the H$_2$SiP system with ab initio and density functional methods. In the wake of recent experimental advances, Driess and Janoschek have also undertaken theoretical studies of H$_2$Si=P=PH and H$_2$Si=P=SiH$_3$.

There appear to be no systematic, experimental studies of the thermochemistry of silicon−phosphorus compounds. To fill this void, we recently calculated the structures, vibrational frequencies, and heats of formation for over 50 Si$_2$P$_n$H$_m$ molecules at the G2 level of theory. This set is a comprehensive collection of all types of Si−P bonding and includes single and multiple bonds, radicals, triplets, silylenes, cyclic systems, and hydrogen-bridged species. A group additivity scheme has been developed that reproduces the heats of formation with a mean absolute deviation of 3.4 kcal/mol and can be used to describe bonding on surfaces and in solids, as well as in the gas phase. Zachariah and Melius have also computed heats of formation for a number of Si−P−H species using the BAC-MP4 method (MP4/6-31G(d,p) with bond additivity corrections). Their results compare well with our more accurate G2 calculations, with an average absolute difference of 2.7 kcal/mol.
mol. The largest error in the BAC-MP4 calculations is 8 kcal/mol for Si=SP. In the present work, we have used the G2 theory to calculate transition states for reactions connecting some of the more stable Si$_3$PH$_n$ species.

**Methods**

Molecular orbital calculations were carried out with the Gaussian 98 series of programs using a variety of basis sets of split valence quality or better with multiple polarization and diffuse functions. Geometries were optimized by second-order Möller–Plesset perturbation theory (MP2(full)/6-31G(d)); a subset representing all of the major bonding motifs was also optimized at the QCISD(frozen core)/6-311G(d,p) level. A quasi-Newton optimization method was used to locate the minima, while the QST2 or QST3 methods were used to locate many of the transition states. When the nature of the transition state was unclear, the reaction path following was used to verify the connectivity. Some of the more difficult transition states were obtained using a combined method for the optimization of both transition states and points along the reaction path. This method starts with an approximate N-point path which is iteratively relaxed until one of the points converges to a transition state, the end points converge to minima, and the remaining points converge to an approximate steepest descent path. In addition to locating transition states that resisted optimization by conventional methods, this approach occasionally identified unexpected intermediates along the path.

Vibrational frequencies and zero-point energies were calculated at the MP2(full)/6-31G(d) level using analytical second derivatives, and thermal corrections to the energies were calculated by standard statistical thermodynamic methods. Correlated energies were calculated by fourth-order Möller–Plesset perturbation theory (MP4SDTQ, frozen core) and by quadratic configuration interaction with perturbative correction for triple excitations (QCISD(T), frozen core) with the MP2(full)/6-31G(d) optimized geometries. Relative energies were computed by the G2 method (modified slightly, in that unscaled MP2 frequencies were used instead of Hartree–Fock, giving results within 0.8 kcal/mol of the regular G2 method). The energy computed at MP4/6-311G(d,p) was corrected for the effect of diffuse functions obtained at MP4/6-311+G(d,p), for the effect of higher polarization functions obtained at MP4/6-311G(2df,p), for the effect of electron correlation beyond fourth order obtained at QCISD(T)/6-311G(d,p), and for the inclusion of additional polarization functions at MP2/6-311+G(3df,2p). Higher level corrections (HLC) for deficiencies in the wave function were estimated empirically by comparing the calculated and experimental bond dissociation energies for 55 well-characterized molecules.

**Results and Discussion**

Figure 1 is a general map of the Si$_2$PH$_n$ reactions considered in this work. Figure 2 shows some of the low-energy pathways from Si$_3$PH to Si$_2$PH$_3$. Structures are grouped according to the number of hydrogens and are labeled with the prefixes A, B, C, and D for $n = 7, 5, 3$, and 1, respectively. Within each of these sets, the labeling indicates the order of increasing energy. Energies are in kcal/mol relative to the lowest energy structure, SiH$_3$+P=SiH$_3$, with H$_2$ molecules used to place the $n < 7$ structures on this scale. Transition states are labeled by the two structures that they connect. Unimolecular reactions are shown in Figures 3–8, with energies relative to the lowest energy isomer in each group. Hydrogen addition reactions appear in Figure 9. The Si–P bond lengths at the QCISD level of theory are on average 0.02 Å (0.8%) longer than the MP2 bond lengths with a standard deviation of 0.03 Å (1.2%), while the average difference in the Si–H and P–H bonds is ca. 0.01 Å (~1%). Since a variety of minima not included in the previous study have been found in this work, atomization energies, heats of formation, and entropies of all the Si$_3$PH$_n$ ($n = 7, 5, 3, 1$) compounds are given in Table 1. Barriers for unimolecular reactions and H$_2$ additions are given in Tables 2 and 3, respectively. The differences between optimization at the MP2 and QCISD levels are examined in Table 4, where it is shown that the relative energies agree to within 0.5 kcal/mol, indicating that the MP2 structures are sufficiently accurate for the present work.

Si$_3$PH$_7$ (Figure 3), Simon et al. have found evidence of these species in the mass spectral analysis of the pyrolysis of a phosphine/disilane mixture in an LPCVD reactor. Disilylphosphine (A1), which contains typical Si–P single bonds (ca. 2.25 Å), is the lowest energy isomer. The corresponding ylide (A3), with one normal and one dative Si–P bond, is 35.8 kcal/mol higher in energy. This is in agreement with results from an earlier study where SiH$_2$PH$_3$ was found to be 34.3 kcal/mol above silylphosphine. These isomers may be formed through the interaction of SiH$_2$ with silylphosphine, SiH$_3$PH$_2$, which itself is produced from the reaction of SiH$_2$ with phosphine and is observed in the copyrolysis of disilane and phosphine. Here, the computed binding energy of SiH$_2$ and silylphosphine to form A3 is 22.3 kcal/mol. This agrees well with binding energies reported for SiH$_2$ + PH$_3$: 21.2 kcal/mol in this work, 18 – 26 kcal/mol in the literature.

Isomer A1 can be reached from A3 via a 1–2 H-shift, transition state (TS) A3→A1, with a 31.0 kcal/mol barrier. This is 9 kcal/mol lower than the analogous SiH$_2$PH$_3$ barrier computed at a simpler level of theory (MP3/6-31G(d)/HF/3-21G) by Dykema et al. However, since the binding energy of SiH$_2$ in A3 is smaller than this barrier height, insertion of SiH$_2$ into a silylphosphine P–H bond may provide a lower energy pathway to A1. For the SiPH$_3$ system, the barrier for SiH$_2$ insertion into a phosphine P–H bond has been computed to be less than 2 kcal/mol.

The SiH$_3$SiH$_2$PH$_2$ isomer (A2) is only 5.3 kcal/mol higher than A1, with no reasonable transition state to provide a connection (other than SiH$_2$ elimination and reinsertion). Isomer A2 is easily reached from the higher energy A4 via a 1–3 H-shift (TS A4→A2) with a barrier of 8.7 kcal/mol. Structure A4 can be formed from SiH$_2$ and silylenephosphorane with a binding energy of 35 kcal/mol. As silylene accepts the silicon lone pair, the structure of the ylide moiety changes relatively
little. The H–Si–H angle widens by 8° and electron density in the Si–P bond shifts toward the silicon, increasing the bond length by 0.024 Å. Dissociation of A4 into the products PH3 + SiH2 occurs with a small barrier, 4.5 kcal/mol, and is slightly exothermic, −1.3 kcal/mol.

Si2PH5. As shown in Figure 4, the lowest energy Si2PH5 isomer is a cyclic three-membered ring, B1. Only 2.3 kcal/mol above this is a phosphasilene, H3SiP=SiH2 (B2), with a silicon–phosphorus double bond. Driess et al. have synthesized compounds of the form B2 with a variety of substituents, including bulky sterically stabilizing groups, and have characterized them spectroscopically, chemically, and computationally.13,27,41 Some of these compounds were found to be stable up to 90 °C.41c This is in good accord with one of the key findings of the present study, namely that the Si= P structure B2 is calculated to be relatively stable with respect to unimolecular decomposition and rearrangement. Several pathways (Scheme 1) for the unimolecular reactions can be contemplated: simple bond cleavage, H2 and SiH2 eliminations, and 1–2 and 1–3 hydrogen shifts. Elimination of H2 is endothermic by ca. 20 kcal/mol and has an overall barrier of 50 kcal/mol, as discussed below. Silylene elimination is endothermic by 60 kcal. The Si–P single- and double-bond cleavages are endothermic by 50 and 80 kcal/mol, respectively. Because these reactions are very endothermic, the related barriers were not examined as part of this study. This leaves hydrogen shift reactions as the most feasible routes for unimolecular reaction.

SCHEME 1

Conversion of B2 to B1 via a 1–2 H-shift across the Si–P single bond is impeded by a 33 kcal/mol barrier. In this ring-closing reaction (B2–B1), the Si–Si bond is almost fully formed in the TS, being only 0.03 Å longer than a typical acyclic Si–Si single bond. The shifting H atom is still significantly bonded to the silicon, but the Si–P bond is partially broken in the TS, with the distance 0.26 Å longer than a typical Si–P single bond. A 1–2 H-shift across the double bond (B2–B6) encounters an even larger barrier of 40 kcal/mol. The product of this reaction, B6, is discussed later in the text.

The smallest barrier from B2 is 16 kcal/mol and leads to a symmetric H-bridged structure (B5) which lies only 4 kcal/mol below the B2–B5 transition state. At the highest level of theory used in the present work, this reaction is considerably more facile than predicted by Driess and Janoschek27 (27 and 9 kcal/mol for the forward and reverse barriers, respectively, computed with pseudopotentials at the MP2 level of theory). Driess et al.41a also found a similar intermediate with fluorine in the bridging position in a theoretical examination of the 1–3 sigmatropic shift of fluorine in FH3Si=SiH2.

Another phosphasilene, B3, with the silyl substituent on the silicon, lies less than 5 kcal/mol above B2. The Si= P bond is ca. 0.02 Å longer than the double bond of B2 but is still in the range of 2.062–2.094 Å found for Si= P in phosphasilene crystal structures.11–13 The stability of B3 is also comparable to that of B2 with a 39 kcal/mol barrier separating it from the lowest energy isomer. This transition state, B3–B1, involves a 1–2 hydrogen shift across the Si–Si single bond combined with ring closure. As the H atom transfers to the central silicon and breaks the Si–P double bond, it causes partial lone-pair density to appear on both the terminal Si and P. A bond then forms between these two atoms and the ring closes.

The lowest TS found from B3, 25 kcal/mol, connects to B6 via a 1–2 silyl shift that is similar to the 1–2 H-shift separating B6 and B2 but has a relative energy that is 10 kcal/mol lower.

This SiH1–PH=SiH structure is 14.2 kcal/mol above B2 (SiH1= P=SiH2), in agreement with the previous study on both these and the related H2P–SiH and HP=SiH2 compounds, where the energy difference was found to be 13.8 and 14.3 kcal/mol, respectively.

Structure B6 converts readily via B4 to the lowest energy isomer, B1, with an overall barrier of only 2 kcal/mol. This provides alternate pathways from the phosphasilenes B2 and B3 to B1. In the case of B2, the overall barrier is 7 kcal/mol higher than the direct reaction. However, for B3, the pathway with B6 as an intermediate has a barrier 13.5 kcal/mol lower than the direct reaction.

The 1–3 H shift in the reaction B6–B1 is similar to the 1–3 sigmatropic H-shift, B2–B2′, in that an H-bridged intermediate is encountered (in the latter case B5 and in the present case B4). This structure has two types of Si–P single bonds. One
bond is roughly 0.06 Å shorter than a normal Si–P single bond, indicative of some double-bond contribution from the phosphorus lone pair. The other bond is about 0.02 Å shorter than the 2.35 Å dative bonds found in A3 and A4. This suggests that the structure could be a complex of H2Si=PH and SiH2; however the binding energy is too high (50 kcal/mol) and there is substantial lone-pair density on the phosphorus.

The H-bridge in B4 can be broken in two distinct places. Breaking the short Si–H bond gives rise to a 6.5 kcal/mol barrier leading to the lowest energy isomer, B1. As the H atom moves from the bridging position, both of the Si–P bonds become ca. 0.02 Å shorter. The shortening of the partial double bond in the TS occurs because the Si–Si bonding is not yet significant even though the Si–H bridge is already broken. Breaking the longer Si–H bond in B4 leads to some difficulties. The MP2 level of theory predicts B6 to be 1.1 kcal/mol lower in energy than B4 with a 3.5 kcal/mol barrier. However, optimization at the QCISD/6-311G(d,p) level places B6 1.3 kcal/mol above B4 with a smaller 1.7 kcal/mol barrier, while the more highly correlated G2 method places both B4 and the TS

Figure 1. Equilibrium structures for Si2PHn optimized at the MP2(full)/6-31G(d) level of theory. Energies relative to A1 were computed at the G2 level of theory with MP2(full)/6-31G(d) zero-point corrections.
The barrier to complete the reaction, \(B_1\), is 7 kcal/mol higher and has a slightly longer Si–P double bond. The Si–P single bond is longer as well and there is substantial Si–Si double-bond character. This structure is well separated from \(C_1\) by a 20 kcal/mol barrier for the 1–2 H-shift across the Si–Si bond. In this reaction, lone-pair density appears on the doubly bonded silicon as the transferring hydrogen bends toward the opposite silicon. This reduces the Si–Si bond to a single bond and temporarily shifts some of the Si–P double-bond character to the other Si–P bond.

Isomer \(C_3\), \(H_3Si–Si≡P\), has a Si–P triple bond that is 0.013 Å longer than the corresponding bond in \(HSi≡P\). There is an 8 kcal/mol barrier for a 1–2 siyl shift to form \(C_1\). In the \(C_3–C_1\) transition state, the linear Si–Si–P angle bends to 95°, the Si–Si bond lengths by 0.04 Å, and the Si–P triple bond shortens by 0.01 Å before it undergoes the overall 0.072 Å increase to a double bond. Although the Si–P multiple bonds in this system are longer than those in the \(HSiP\) system, differences between the double- and triple-bond lengths are essentially the same, resulting in similar energetics. Isomers \(C_3\) and \(C_1\) are 12 kcal/mol apart, comparable to the 10 kcal/mol difference found in the \(HSiP\) system. 28

The next lowest structures, isomers \(C_4\) and \(C_5\), lie 14–15 kcal/mol above \(C_1\). The three-membered ring, \(C_5\), readily undergoes a 1–2 H-shift from the phosphorus to the SiH group to form \(C_1\) with only a 1 kcal/mol barrier. This reaction is facilitated by the shortening of the opposite Si–P bond in the TS as it converts to a double bond in the product. A larger barrier of 8 kcal/mol was found for the 1–2 shift in the opposite direction to form \(C_2\). Although a Si–P double bond is formed in this reaction as well, the barrier is larger because the H-shift occurs across this bond, lengthening it in the TS. In reverse, this reaction provides a pathway, \(C_2–C_5–C_1\), that has an overall barrier 4 kcal/mol lower that the 20 kcal/mol barrier for the direct \(C_2–C_1\) reaction. The doubly H-bridged form, \(C_4\), is reasonably stable, being separated from \(C_1\) and \(C_5\) by barriers of 24 and 11 kcal/mol, respectively. In the \(C_4–C_5\) transition state, both bridging H atoms transfer simultaneously to one of the silicon atoms. A similar barrier of 10 kcal/mol is found for the conversion of the singly H-bridged \(C_6\) to the 2 kcal/mol higher three-membered ring, \(C_7\).

In the \(C_6–C_7\) TS, the Si–Si bond forms as one H–Si bond breaks and the corresponding Si–P bond lengthens. This becomes a dative bond, while both Si–Si and \(HSi≡P\) take on partial double-bond character in the product, \(C_7\). This isomer is also relatively stable, with a 12 kcal/mol barrier for the reaction \(C_7–C_5\), a 1–2 H-shift from the phosphorus across the short Si–P bond. This bond is broken in the TS as the PH2 group tips toward SiH. Meanwhile, the dative Si–P bond lengthens by 0.06 Å and the Si–Si double-bond character increases. Once the hydrogen is transferred, both Si–P distances
shorten to partial double bonds and Si–Si lengthens to a single bond. As discussed above, transfer of the second hydrogen in PH$_2$, C5–C1, is much more facile.

Three closely related structures were found 33–34 kcal/mol above C1 (Figure 7). In these isomers, C9 through C11, each heavy atom is bonded to one hydrogen. The symmetric anti-anti structure, C9, has a 5 kcal/mol barrier separating it from C11. The anti,syn isomer of C9, which is 0.8 kcal/mol higher in energy, is an intermediate on the path. At the G2 level of theory, the C11–C10 barrier disappears. (The MP2(full)/6-31G-
(d) barrier is 2 kcal/mol, while at QCISD/6-31G(d) it is only 0.5 kcal/mol.) These structures can readily convert to the second lowest energy isomer, $C_2$, through the reaction $C_1$, a $1\rightarrow 3$ H-shift accompanied by ring closure, with a 5 kcal/mol barrier.

**Si$_2$PH (Figure 8).** The lowest energy isomer, $D_1$, is a four-membered ring with the H atom bridging the two Si atoms. The related nonbridged $D_2$ is 8.5 kcal/mol higher in energy.

This structure is reasonably stable with a 18 kcal/mol barrier for insertion of the H atom into the Si–Si bond. Isomer $D_3$, with two partial Si–P double bonds and an unusually long Si–Si single bond, is 11.5 kcal/mol above $D_2$ and is separated from it by an 8 kcal/mol barrier.

**Unimolecular Reactions.** The assorted unimolecular reactions discussed above are classified in Table 2, written in the exothermic direction. The $1\rightarrow 2$ hydrogen shifts can be separated into two categories according to both barrier height and reactant type. The highest barriers, 24–38 kcal/mol, were found for cases in which the reactants were either acyclic or hydrogen-bridged structures. For some reactions, such as $B_6\rightarrow B_2$ and the H-bridged $C_4\rightarrow C_1$, the barrier is lower than expected for a $1\rightarrow 2$ H-shift because of exothermicity, which contributes to decreasing the barrier height. Lower barriers of 1–20 kcal/mol were found for reactants with cyclic Si–P–Si frameworks. These reactions may also be described as $1\rightarrow 3$ H-shifts, which typically have lower barriers than $1\rightarrow 2$ H-shifts. The highest barrier, 20 kcal/mol, was found for $C_2\rightarrow C_1$, the only case in which a cyclic...
reactant possesses a full Si–P double bond, giving it extra stability. The lowest barrier, 1 kcal/mol, occurred for C5–C1, the most exothermic of the cyclic 1–2 H-shifts. Barriers for hydrogen bridge formation by insertion into a Si–Si bond, 8–18 kcal/mol, fall into the same range as the 1–2 H-shifts with cyclic reactants. This is not surprising, since these reactions are essentially 1–2 shifts with the H-bridged structures formed as lower energy intermediates between cyclic reactants and their mirror image isomers. Reactions that break an H-bridge to form a lower energy product occur more easily, with barriers of 1.7–6.5 kcal/mol. The 1–3 H-shifts listed in Table 2 all involve transfer of the hydrogen from the phosphorus on an acyclic P–Si–Si frame.

H2 Addition Reactions. The Si3PH3 isomers with differing numbers of hydrogens are connected by H2 addition reactions as shown in Figure 9 and Table 3. The simplest model for H2 addition is SiH2 + H2 → SiH4. Jasinkski and Chu performed an RRKM analysis of their pressure-dependent study of the SiH2 + H2 reaction and found the results at 300 K to be consistent with the 1.7 kcal/mol barrier computed by Gordon et al. at the MP4/6-31G++(3df,3pd)//MP2/6-31G(2d,2p) level of theory. More detailed RRKM analyses of the data indicated a lower activation energy of 0.3 kcal/mol. Using various density functional methods, Sosa and Lee predict the SiH2 + H2 barrier to be 3.52 kcal/mol. Calculations at the QCISD(T)/6-311++G(d,p)//MP2/6-31G(d,p) level of theory give a barrier of 4.2 kcal/mol, while the G2 method, which is an
approximation of this level of theory, gives a value of 3.9 kcal/mol. At the estimated QCISD(T)/6-311++G(3df,3pd) level of theory, the barrier is 2.9 kcal/mol. Thus, on the basis of SiH₂ + H₂, one would expect very facile 1,1-addition of H₂ to unsaturated silicon in Si₂PH₄. However, as discussed below, this is not necessarily the case when there is significant interaction with neighboring groups.

The transition state with the lowest overall energy found connecting Si₂PH₄ to Si₂PH₅ lies between the lowest energy forms, D1 and C1, with a 24 kcal/mol barrier. This TS occurs
was verified by the reaction path optimization technique which is only 1 kcal/mol lower than that of 17.9 kcal/mol found between C5 and C6.

TABLE 1: Atomization Energies, Heats of Formation, and Entropies at the G2 Level of Theory

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<td>C8</td>
<td>SiH2-P-SiH</td>
<td>345.2</td>
<td>101.3</td>
</tr>
<tr>
<td>C9</td>
<td>SiH2-P-SiH</td>
<td>343.7</td>
<td>102.7</td>
</tr>
<tr>
<td>C10</td>
<td>SiH2-P-SiH</td>
<td>343.0</td>
<td>103.5</td>
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<tr>
<td>C11</td>
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<td>342.7</td>
<td>103.8</td>
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<tr>
<td>D1</td>
<td>SiH2-P-Si</td>
<td>255.7</td>
<td>87.5</td>
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<tr>
<td>D2</td>
<td>SiH2-P-Si</td>
<td>247.4</td>
<td>95.8</td>
</tr>
<tr>
<td>D3</td>
<td>SiH2-P-Si</td>
<td>236.0</td>
<td>107.2</td>
</tr>
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</table>

Cyclic and hydrogen-bridged structures are designated by e and hb, respectively. H-bridged species are four-membered rings unless otherwise noted. * The H-bridge is across the Si-Si bond, making a three-membered ring. † In kcal/mol with MP2(full)/6-31G(d) zero-point energies scaled by 0.9646. ‡ Heats of formation at 0 and 298 K are referred to the following values in kcal/mol: 51.63 and 52.10 for H, 75.42 and 75.62 for P, 108.1 and 109.1 for Si. § Thermal corrections were computed using unscaled MP2(full)/6-31G(d) frequencies. ‖ In cal/(mol K).

relatively early in the reaction, with the H−H bond 0.25 Å shorter and Si−H bonds 0.15−0.17 Å longer than the corresponding bonds in the SiH2 + H2 transition state. The TS for H2 addition to D2 is 12 kcal/mol higher in energy. This reaction, with a 28 kcal/mol barrier, connects D2 to C2 with C8 as an intermediate. The D2−C8 TS occurs later in the reaction than for D1−C1, with shorter Si−H and longer H−H distances. The H-bridged intermediate C8, formed by insertion of one of the adding H atoms into the Si−Si bond, is 22.5 kcal/mol below this TS. However, the barrier to break the H-bridge and reclose the ring is less than 4 kcal/mol. The D2−C8−C2 connectivity was verified by the reaction path optimization technique which encountered C8 as an intermediate minimum in the attempt to find a TS between D2 and C2. Addition of H2 to isomer D3 has the smallest barrier height, 15 kcal/mol. However, the overall energy of the TS, D3−C5, is only 1 kcal/mol lower than that of D2−C8. The barriers for H2 addition to the Si2P3H2 isomers are much larger than the experimental 0.3−1.7 kcal/mol barrier for SiH2 insertion into H2 as the “empty” silicon p orbital actually contains significant electron density as evidenced by the partial Si−P double bonds in D1−D3. The barrier for H2 addition to D2 is, however, ca. 10 kcal/mol smaller than the barrier for 1,2-addition of H2 across a similar Si−Si double bond in disilene (39.5 kcal/mol, MP4/6-31G(d,p)/MP2/6-31G(d),p).47

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for the low addition barrier to C5 is not as readily apparent. The partial Si–P bond on the reactive silicon in C5 suggests that the barrier should be similar to the 15–18 kcal/mol barriers found for H2 addition to the Si3PH isomers. However, in the C5–B4 TS, the partial Si–P double bond becomes 0.12 Å longer than a typical Si–P single bond. This behavior gives rise to the small 2 kcal/mol barrier and is related to the formation of the H-bridge in the product, B4, which, as discussed above, can readily isomerize to B1 with a barrier of 6.5 kcal/mol. In C9, the alllylic nature of the π system, with partial Si–P double bonds, hinders H2 addition, giving rise to a 16 kcal/mol barrier. An even larger barrier of 26 kcal/mol is found for H2 addition to C2, where the silicon reaction site is not electron deficient. Here the Si–P double bond must be broken before H2 can interact with the silicon p orbital.

Two H2 addition reactions were found connecting Si3PH2 to Si3PH3. The smallest barrier, 11 kcal/mol, is for B6–A1, forming the lowest energy structure SiH3PHSiH3. This is 5.7 kcal/mol smaller than the barrier for the addition to the allylic C9. However, the barrier does not vanish since there is still substantial Si–P double bond character on the reactive silicon. The reverse barrier of 55 kcal/mol for B6–A1, the 1,1-elimination of H2 from SiH3PHSiH3, agrees well with the 58 kcal/mol barrier found by Mains et al.22 for H2 elimination from SiH2PH2. The second reaction, B5–A2, involves hydrogen addition to phosphorus combined with ring opening. In this TS, with a 26 kcal/mol barrier, the bridging H transfers to one of the silicon atoms and the corresponding Si–P bond breaks before any significant interaction occurs between the phosphorus atom and the adding hydrogens.

Conclusions

This study has examined the stability of 29 minima in the Si3PHn (n = 5, 7, 8, 9, 10) system with respect to unimolecular rearrangement and H2 addition. Compounds in this work include examples of silicon–phosphorus multiple bonds and hydrogen bridging. Structures B2, B3, C1, and C2 contain silicon–phosphorus bonds that lie within the range of 2.062–2.094 Å found for Si–P double bonds in crystal structures11–13 and are particularly stable with respect to unimolecular rearrangement. The phosphasilenes B2 and B3 have barriers in excess of 25 kcal/mol along both direct and indirect routes to B1, the lowest energy Si3PH2 structure. The cyclic structure C2 is separated from C1, the lowest of the Si3PH3 isomers, by barriers of 16–20 kcal/mol. Structures containing partial Si–P double bonds are typically less stable, as exemplified by the comparison of the 1–3 H-shifts from the silyl groups in SiH3–PH=SiH (B6) and SiH1–PH=SiH2 (B2). In each case, there is an H-bridged intermediate (B4 and B5, respectively) from which the barrier to completion is 4–5 kcal/mol. However, the former case has only a partial Si–P double bond and B6 is predicted to collapse with no barrier to the intermediate B4. In the latter, B2 has a full double bond and B2–B5 is endothermic with a 16 kcal/mol barrier.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE 9400678).

Supporting Information Available: Listings of Cartesian coordinates and energies for the minima and transition states at the MP2(full)/6-31G(d) level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


