Structures and Energetics of Some Silicon−Phosphorus Compounds: SiH_mPH_n, $SiH_mPH_nSiH_o$, and $(SiH_3)_3P$. An ab Initio Molecular Orbital Study

Anwar G. Baboul and H. Bernhard Schlegel*

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202-3489

Received March 11, 1996. Revised Manuscript Received June 21, 1996[⊗]

Abstract: The geometries of 48 isomers of SiH_mPH_n ($m + n = 0-5$), $SiH_mPH_nSiH_o$ ($m + n + o = 0-7$), and $(SiH_3)_3P$ have been optimized at the MP2/6-31G(d) level of theory. Silylenes and cyclic structures dominate the compounds with low numbers of hydrogens; nevertheless, there are several examples of silicon−phosphorus multiple bonding. Relative energies, heats of formation, and bond dissociation energies have been calculated at the G2 level of theory. Two empirical schemes have been constructed to fit the atomization energies. A simple bond additivity approach reproduces the data with a mean absolute deviation of 5.3 kcal/mol. Better results are obtained with a group additivity scheme which gives a mean absolute deviation of 3.4 kcal/mol.

Introduction

Compared to other aspects of silicon chemistry, surprisingly little is known about the chemistry of SiP bonds. A number of interesting examples of SiP bonding and reactivity can be found in inorganic, organic, and organometallic chemistry.[1] Silicon−phosphorus bonding is also relevant to chemical vapor deposition of phosphorus-doped silicon for semiconductors.[2] With this ab initio molecular orbital study, we hope to contribute to the understanding of the structure and energetics of some simple silicon−phosphorus compounds.

Of the parent single-bonded silicon−phosphorus species, silylphosphine has been studied by microwave spectroscopy[3] and photoelectron spectroscopy;[4] trisilylphosphine has been examined by electron diffraction[5] and X-ray crystallography.[6] The structures of about 200 SiP compounds have been determined by X-ray crystallography.[7] A few of the more interesting ones include Si−P analogues of cyclobutane,[8] bicyclobutane,[9] spiropentane,[10] hexane,[11] norbornane,[12] adamantane,[13] and cubane.[14] Some of these, along with simpler silylphosphines, have found uses as ligands in transition metal complexes.[1,7] Silicon−phosphorus single bonds are remarkably reactive.[1] They react readily with water, oxygen, carbon dioxide, halogens, halides, etc. However, there appears to be no systematic study of the experimental thermochemistry of silicon−phosphorus compounds.[15]

Far less is known about Si═P double bonds.[16] Thermal decomposition of substituted 2-silaphosphetane is thought to give an Si═P intermediate which dimerizes rapidly.[17] Bulky groups stabilize the double bond, making it possible to characterize these compounds spectroscopically and to study their reactivity.[18] This approach has recently culminated in the first X-ray crystal structures of compounds containing Si═P double bonds.[19,20]

A number of calculational studies have examined various aspects of silicon−phosphorus bonding. Gordon and coworkers[21] carried out HF/3-21G* calculations on $SiPH_5$, $SiPH_3$, and SiPH as prototypes of single, double, and triple SiP bonds. Cowley and collaborators[22] studied various isomers of $SiPH_3$ at the HF/6-31G** level of theory to explore the stability of Si═P double bonds. Schleyer and Kost[23] calculated the bond energy of $H_2Si{=}PH$ in a comparison of double bond energies of second-row elements with carbon and silicon. Raghavachari

⊗ Abstract published in *Advance ACS Abstracts*, August 1, 1996.

(1) Armitage, D. A. In *The Silicon−Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; J. Wiley: New York, 1989, p 151; 1991, p 183.
(2) Jasinski, J. M.; Meyerson, B. S.; Scott, B. A. *Annu. Rev. Phys. Chem.* **1987**, *38*, 109.
(3) Varma, R.; Ramaprasad, K. R.; Nelson, J. F. *J. Chem. Phys.* **1975**, *63*, 915.
(4) Cradock, S.; Ebsworth, E. A. V.; Savage, W. J.; Whiteford, R. A. *J. Chem. Soc. Faraday Trans. 2* **1972**, *68*, 934.
(5) Beagley, B.; Robiette, A. G.; Sheldrick, G. M. *J. Chem. Soc. A* **1968**, 3002.
(6) Blake, A. J.; Ebsworth, E. A.; Henderson, S. G. D. *Acta Crystallogr.* **1991**, *C47*, 486.
(7) Cambridge crystal structure database: Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187.
(8) Clegg, W.; Haase, M.; Klingebiel, U. K.; Sherldrick, G. M. *Chem. Ber.* **1983**, *116*, 146.
(9) Driess, M.; Pritzkow, H.; Reisgys, M. *Chem. Ber.* **1991**, *124*, 1923.
(10) Tebbe, K.-F.; Heinlein, T. *Z. Anorg. Allg. Chem.* **1984**, *515*, 7.
(11) Driess, M.; Reisgys, M.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1510.
(12) Honle, W.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1978**, *442*, 107.
(13) Honle, W.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1978**, *442*, 91. Baudler, M.; Oehlert, W.; Tebbe, K.-F. *Z. Anorg. Allg. Chem.* **1991**, *598*, 9.
(14) Baudler, M.; Scholz, G.; Tebbe, K.-F.; Feher, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 339.
(15) Walsh, R. *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; J. Wiley: New York, 1989; p 151.
(16) Driess, M.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 828.
(17) Couret, C.; Escudie, J.; Satge, J.; Andriamizaka, J. D.; Saint-Roche, B. *J. Organomet. Chem.* **1979**, *182*, 9.
(18) (a) Smith, C. N.; Bickelhaupt, F. *Tetrahedron Lett.* **1984**, *25*, 3011. (b) Smit, C. N.; Bickelhaupt, F. *Organometallics* **1987**, *6*, 1156. (c) van den Winkel, Y.; Bastiaans, H.; Bickelhaupt, F. *J. Organomet. Chem.* **1991**, *405*, 183. (d) Driess, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1022. (e) Driess, M.; Pritzkow, H. *J. Chem. Soc., Chem. Commun.* **1993**, 1585.
(19) Bender, H. R. G.; Niecke, E.; Nieger, M. *J. Am. Chem. Soc.* **1993**, *115*, 3314.
(20) Driess, M.; Rell, S.; Pritzkow, H. *J. Chem. Soc., Chem. Commun.* **1995**, 253.
(21) Dykema, K. J.; Truong, T. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 4535.
(22) Lee, J.-G.; Boggs, J. E.; Cowley, A. H. *J. Chem. Soc., Chem. Commun.* **1985**, 773.
(23) Schleyer, P. v. R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105.

S0002-7863(96)00771-8 CCC: $12.00

et al.[24] investigated the insertion of silylene into various species, including PH_3. Maines et al.[25] examined the 1,1-elimination of H_2 from H_3SiPH_2 to form $HSi{=}PH_2$. A number of authors[26] have calculated ring strain energies of heterosubstituted cyclopolysilanes and have noted that cyclic SiH_2SiH_2PH and other monosubstituted 3-membered polysilane rings have unusually short Si−Si bonds. Nyulászi et al.[27] have calculated $HSiPH_2$ and H_2SiPH in connection with a study of substituent effects on the stability of silylenes and silyl radicals. Schoeller and Busch[28] have computed the cations, radicals, and anions of H_2SiP and $SiPH_2$. In the wake of recent experimental advances, Driess and Janoschek[29] have also undertaken theoretical studies of $H_2Si{=}PH$ and $H_2Si{=}P{-}SiH_3$.

The purpose of the present work is to expand our understanding of the structure and energetics of compounds with one or more SiP bonds. Specifically, we have used ab initio molecular orbital calculations at the MP2/6-31G* level of theory to determine the geometries and relative stabilities of various isomers of SiH_mPH_n ($m + n = 0-5$) and $SiH_mPH_nSiH_o$ ($m + n + o = 0-7$). Heats of formation and bond dissociation energies were then calculated for these isomers at the G2 level of theory,[30] which has been shown to give reliable values that are within ±2 kcal/mol of accurately known experimental energy differences.[31]

Methods

Molecular orbital calculations were carried out with the GAUSSIAN 94[32] series of programs using a variety of basis sets of split valence quality or better with multiple polarization and diffuse functions.[33] Equilibrium geometries were optimized by Hartree−Fock and second-order Møller−Plesset perturbation theory (HF/6-31G(d) and MP2(full)/6-31G(d), respectively) using a quasi-Newton optimization method.[34] Vibrational frequencies and zero-point energies were calculated at the HF/6-31G(d) level using the HF-optimized geometries and analytical second derivatives.[35] Thermal corrections to the energies were calculated by standard statistical thermodynamic methods using the HF/6-31G(d) frequencies. Correlated energies were calculated by fourth-order Møller−Plesset perturbation theory[36] (MP4SDTQ, frozen core) and by quadratic configuration interaction with perturbative correction for triple excitations[37] (QCISD(T), frozen core) with the MP2(full)/6-31G(d) optimized geometries.

Atomization energies were computed by the G2 method,[30] in which the energy computed at MP4/6-311G(d,p) is 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 are estimated empirically[30] by comparing the calculated and experimental bond dissociation energy for 55 well-characterized molecules.

Most of the radicals have S^2 in the range 0.75−0.80, but $R{-}P{=}SiH$, $H_2SiPSiH_2$, and cyclic HSiPSiH have somewhat larger spin contamination (1.1−1.3). Although energies computed with Møller−Plesset perturbation theory are significantly affected by spin contamination, energies calculated with the QCISD(T), CCSD(T), and G2 methods are not.[30,38] Use of the spin-projected MP_n energies in the G2 calculations instead of the unprojected values alters the G2 energies by less than 0.5 kcal/mol, even when there is significant spin contamination.

Results and Discussion

The structures considered in the present work are shown in Figures 1−3. Total energies at the MP2(full)/6-31G*, QCISD(T)/6-311G**, G2MP2, and G2 levels, and harmonic vibrational frequencies calculated at the HF/6-31G* level for all of the structures are listed in the supporting information. Structures with the same number of hydrogen atoms are discussed as a group; within each group, structures are ordered approximately in terms of decreasing stability as calculated at the G2 level of theory. Structures, relative energies, and isodesmic reactions are considered first, followed by a discussion of the heats of formation and dissociation energetics. Unless otherwise stated, all energy differences discussed in the text are calculated at the G2 level of theory.

Geometries and Relative Energies. (a) $SiPH_5$. The MP2/6-31G* optimized geometry of silylphosphine, **1a**, and the corresponding ylide, **1b**, are in good agreement with previous calculations.[20,27] The bond lengths in **1a** are within 0.005 Å of the experimental values from the microwave structure;[3] this suggests that a typical Si−P single bond length is ca. 2.25 Å. The ylide **1b** is 34.3 kcal/mol less stable than silylphosphine, **1a**, and has a significantly longer bond length (2.327 Å). By comparison, the corresponding carbon ylide,[39] CH_2PH_3, is 45.9 kcal/mol higher than methyl phosphine and shows a 0.19 Å shortening of the C−P bond.

(b) $SiPH_4$. Two different isomers can be generated by removing a hydrogen from silylphosphine. Since the Si−H bond energy in SiH_4 (91.3 kcal/mol) is greater than the P−H bond energy in PH_3 (81.5 kcal/mol), it can be anticipated that structure **2b**, SiH_2PH_2 (obtained by breaking an Si−H bond in SiH_3PH_2), is higher in energy than SiH_3PH (obtained by breaking the P−H bond). The *anti* rotomer of SiH_2PH_2 is 1.5 kcal/mol lower than the *gauche*. For SiH_3PH, two states need to be considered. The $^2A''$ state, **2a**, is 7.9 kcal/mol lower than **2b**, has a normal Si−P single bond (2.254 Å), and has a small SiPH angle (93.4°, since the σ lone pair orbital on P is doubly

(24) Raghavachari, K.; Chandrasekhar, J.; Gordon, M. S.; Dykema, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 5853.
(25) Maines, G. J.; Trachtman, M.; Bock, C. W. *Theochem* **1991**, *231*, 125.
(26) (a) Grev, R. S.; Schaefer, H. F. *J. Am. Chem. Soc.* **1987**, *109*, 6577. (b) Cremer, D.; Gauss, J.; Cremer, E. *Theochem* **1988**, *169*, 531. (c) Boatz, J. A.; Gordon, M. S. *J. Phys. Chem.* **1989**, *93*, 3025.
(27) Nyulászi, L.; Belghazi, A.; Szétsi, S. K.; Veszprémi, T.; Heinicke, J. *J. Mol. Struct. (Theochem)* **1994**, *313*, 73.
(28) Schoeller, W. W.; Busch, T. *J. Mol. Struct. (Theochem)* **1994**, *313*, 27.
(29) Driess, M.; Janoschek, R. *J. Mol. Struct. (Theochem)* **1994**, *313*, 129.
(30) (a) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221. (b) Curtiss, L. A.; Carpenter, J. E.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1992**, *96*, 9030.
(31) Raghavachari, K.; Curtiss, L. A. In *Modern Electronic Structure Theory Part II*; Yarkony, D. R., Ed.; World Scientific Pub.: Singapore, 1995; p 991.
(32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A.; GAUSSIAN 94; Gaussian, Inc.: Pittsburgh, PA, 1995.
(33) Hariharan, P. C.; Pople, J. A. *Theor. Chem. Acta* **1973**, *28*, 213 and references cited therein. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654. Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265 and references cited therein. The 6-31G(d) and 6-31G(d,p) basis sets are the same as 6-31G* and 6-31G**, respectively.
(34) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214. Peng, C.; Ayala, P. Y.; Schlegel, H. B.; Frisch, M. J. *J. Comput. Chem.* **1996**, *1*, 49.
(35) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1979**, *13*, 225.
(36) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
(37) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.
(38) Chen, W.; Schlegel, H. B. *J. Chem. Phys.* **1994**, *101*, 5957.
(39) G2 energies at 0 K for CH_2PH_3, propane, cyclopropane, and *anti*-$SiH_3SiH_2PH_2$ are −381.832856, −118.855804, −117.631143, and −923.186150 au, respectively.

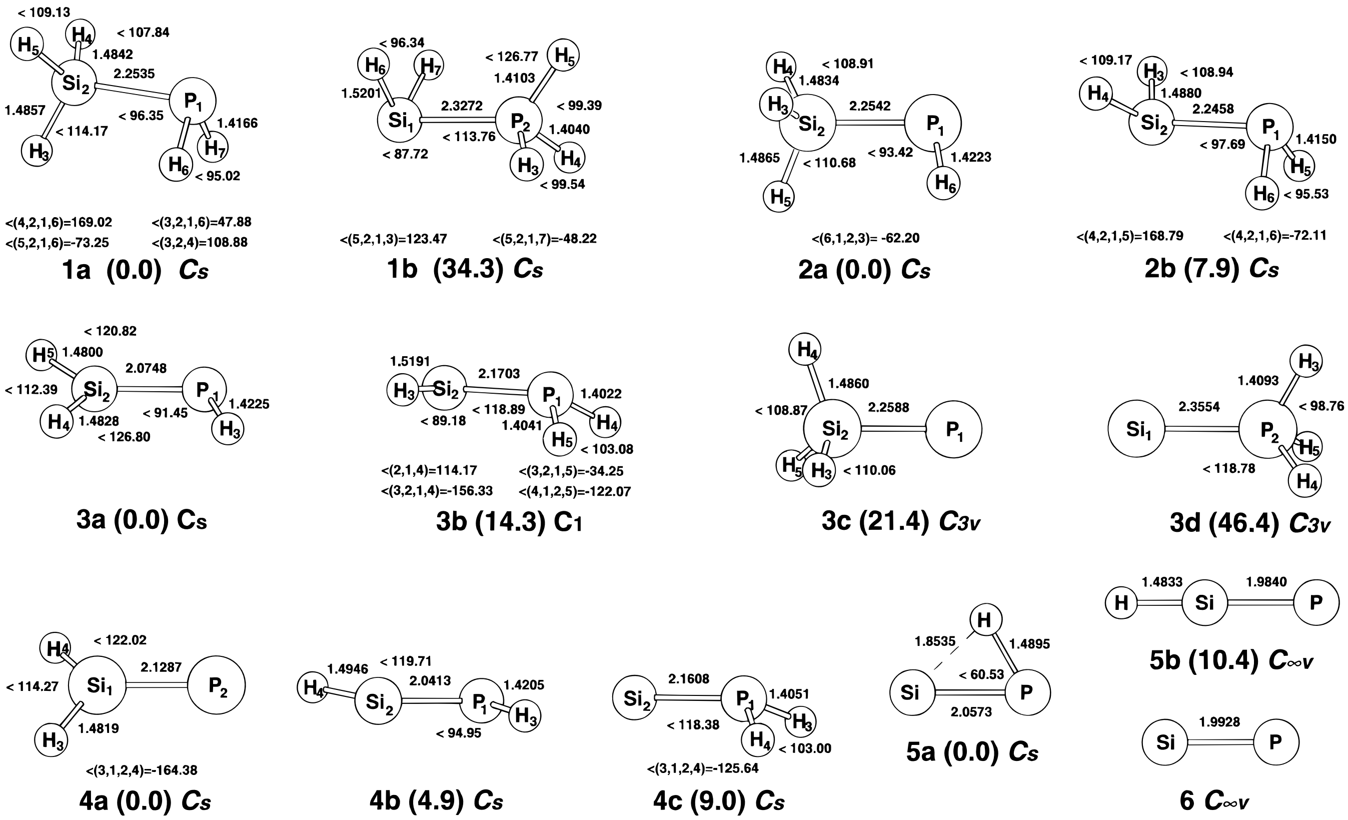


Figure 1. Equilibrium geometries for $SiPH_n$ optimized at the MP2(full)/6-31G(d) level of theory and relative energies of isomers computed at the G2 level of theory.

occupied). The $^2A'$ state is 38.6 kcal/mol higher than the $^2A''$ state, has a short Si−P bond (2.194 Å, because of partial π bonding between phosphorus and silicon), and has a larger SiPH angle (127.8°, since the σ "lone pair" orbital is singly occupied). By comparison, the $^2A_1$ state of PH_2 is calculated to be 53.0 kcal/mol higher than the $^2B_1$ state (experimental, 52.3 kcal/mol[40]) and has a HPH angle of 121.2° (experimental, 123.2° [40]).

(c) $SiPH_3$. Because this set of isomers contains the simplest example of a Si═P double bond, it has been studied by a number of groups.[20−22,27,29] Our findings are in good accord with previous results. The planar structure, **3a**, has the lowest energy in this set. The Si═P double bond length is 2.075 Å, in good agreement with the experimental value of 2.094 Å determined by X-ray crystallography on a sterically stabilized Si═P double bond.[19] An estimate of the π-bond energy of Si═P can be obtained from the rotational barrier of $H_2Si{=}PH$, 28−34 kcal/mol.[29] Another estimate of the π-bond energy can be calculated from the following isodesmic reaction:[23]

$$SiH_3 + PH_2 + SiH_3{-}PH_2 \rightarrow SiH_2{=}PH + SiH_4 + PH_3 \qquad -37.9\ \text{kcal/mol}$$

$$2SiH_3 + SiH_3{-}SiH_3 \rightarrow SiH_2{=}SiH_2 + 2SiH_4 \qquad -32.7\ \text{kcal/mol}^{41}$$

Although the SiP π bond is a bit stronger than the SiSi π bond, the overall double bond strength for Si═P is somewhat less than that of Si═Si (e.g. 101 kcal/mol for $SiH_2{=}PH \rightarrow {}^3SiH_2 + {}^3PH$[42] vs 106 kcal/mol in $SiH_2{=}SiH_2 \rightarrow 2\ {}^3SiH_2$[41]) because Si−P σ bonds are weaker than Si−Si σ bond (e.g. 70 kcal/mol in SiH_3PH_2 versus 76 kcal/mol in SiH_3SiH_3).

The next most stable structure is the silylene **3b**, $SiHPH_2$, which can be derived from SiH_3PH_2 by 1,1-elimination of H_2. In keeping with the effect of electronegative substituents on silylenes, **3b** is stabilized relative to unsubstituted silylene:[44]

$$SiH_2 + SiH_3SiH_3 \rightarrow SiH_4 + SiH_3SiH \qquad -0.7\ \text{kcal/mol}$$

$$SiH_2 + SiH_3PH_2 \rightarrow SiH_4 + SiHPH_2 \qquad -8.5\ \text{kcal/mol}$$

$$SiH_2 + SiH_3Cl \rightarrow SiH_4 + SiHCl \qquad -9.8\ \text{kcal/mol}^{46}$$

Silylene **3b** is only 14.3 kcal/mol higher than $SiH_2{=}PH$, **3a**. The phosphorus is significantly less pyramidal than usual (sum of the valence angles at P is 336.1°) and the barrier to inversion is very low;[27] in addition, the Si−P bond length, 2.170 Å, is intermediate between typical single and double Si−P bonds (2.25 and 2.07 Å, respectively). These facts are consistent with a partial, dative π bond between the lone pair on P and the empty p orbital on Si that contributes to the ca. 8.5 kcal/mol stabilization of the silylene.

(40) Berthou, J. M.; Pascat, B.; Guenebaut, H.; Ramsay, D. A. *Can. J. Phys.* **1972**, *50*, 2265.

(41) Curtiss, L. A.; Raghavachari, K.; Deutsch, P. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *95*, 2433.

(42) Homolytic cleavage of the double bond in $SiH_2{=}PH$ would yield two unpaired electrons on SiH_2 (one from breaking the σ bond and one from breaking the π bond) and likewise two unpaired electrons on PH. Thus triplet SiH_2 and triplet PH are the proper products if one is interested in the double bond strength. For further discussion see refs 43−45.

(43) Janoschek, R. In *Organosilicon Chemistry, from Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH Pub.: Weinheim, 1994; p 84.

(44) Gordon, M. S.; Francisco, J. S.; Schlegel, H. B. *Adv. Silicon Chem.* **1993**, *2*, 137.

(45) Grev, R. S. *Adv. Organomet. Chem.* **1991**, *33*, 125.

(46) Su, M.-D.; Schlegel, H. B. *J. Phys. Chem.* **1993**, *97*, 8732.

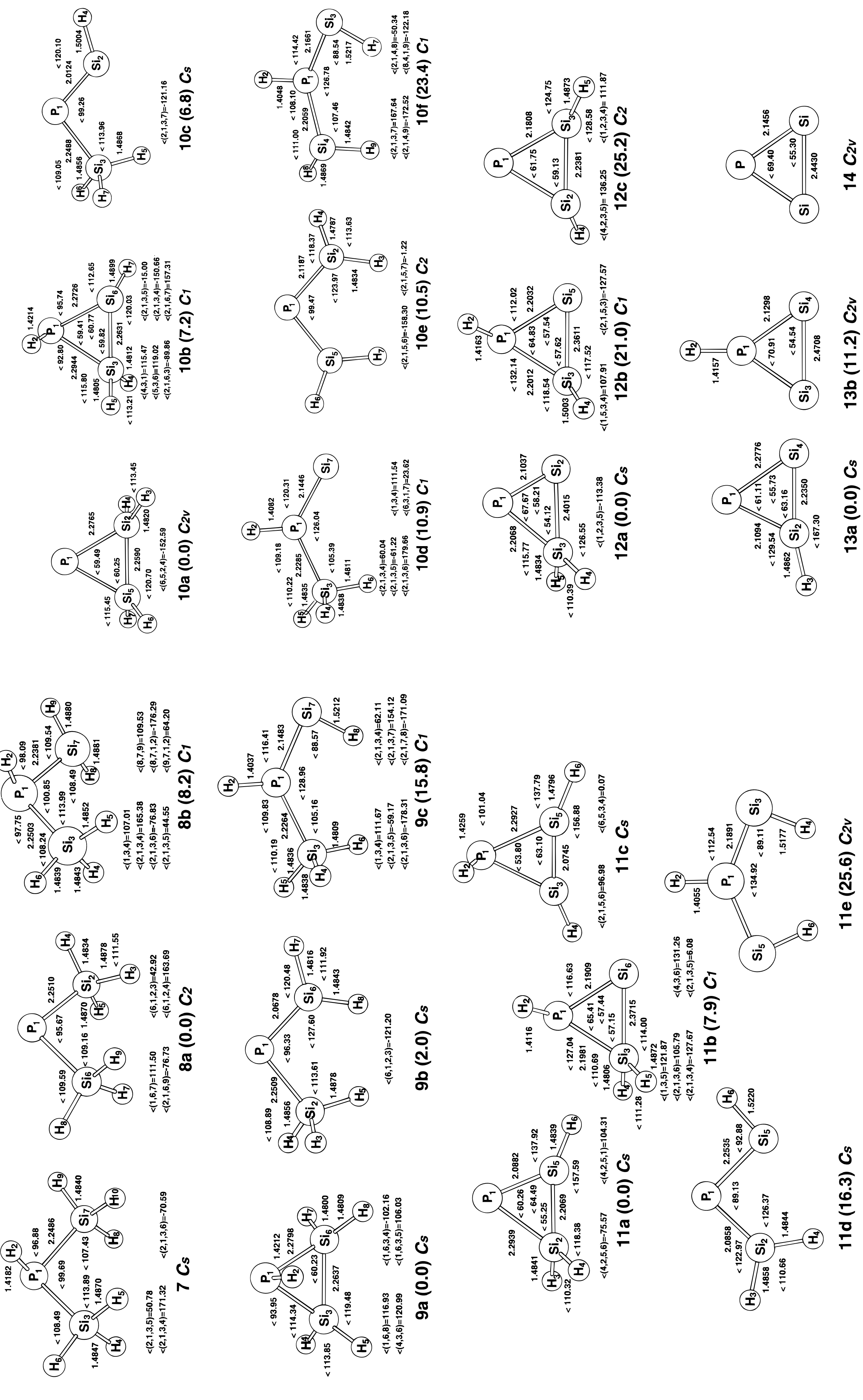
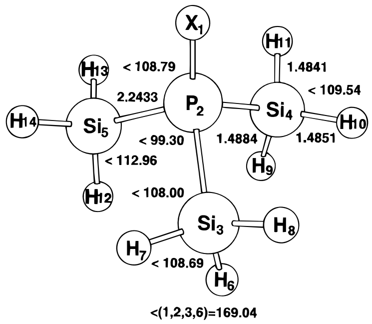


Figure 2. Equilibrium geometries for Si_2PH_n optimized at the MP2(full)/6-31G(d) level of theory and relative energies of isomers computed at the G2 level of theory.



15 ***C3***

Figure 3. Equilibrium geometry for $(SiH_3)_3P$ optimized at the MP2(full)/6-31G(d) level of theory. (X is a dummy atom on the $\mathbf{C_3}$ axis.)

Structure **3c**, SiH_3P, is a ground state triplet with C_{3v} symmetry that lies 21.4 kcal/mol higher than **3a**. It has an typical Si−P single bond and can be derived from **1a** by breaking two P−H bonds. Structure **3d**, $SiPH_3$, is also a ground state triplet and is 46.4 kcal/mol above **3a**.

(d) $SiPH_2$. Compounds **4a**, $H_2Si{=}P$, and **4b**, SiH=PH, can be obtained by breaking an Si−H or P−H bond in $H_2Si{=}PH$; as expected, each structure is planar and has a Si−P double bond. The $H_2Si{=}P$ isomer is 4.9 more stable than *trans* HSi=PH which is 3.9 kcal/mol more stable than *cis* HSi=PH. A different isomer, $Si{=}PH_2$ **4c**, is 9.0 kcal/mol higher than **4a**; it has a nonplanar phosphorus (sum of valence angles at P is 339.8°) and an Si−P bond that is intermediate between a single and a double bond. It is analogous to silylene **3b**, $HSiPH_2$, and can be obtained from the latter by breaking a Si−H bond.

(e) SiPH and SiP. Linear HSiP, **5b**, has a SiP triple bond (1.984 Å), and by comparison with HCN, it would be expected to be the most stable isomer. However, Gordon and co-workers[21] have previously shown that a hydrogen-bridged structure is lower in energy. This is reminiscent of Si_2H_2 which also has a bridged geometry.[47] Bridged Si(H)P, **5a**, has an Si=P double bond, a PH single bond, and a partial SiH bond. At the G2 level of theory it is 10.4 kcal/mol more stable than HSi≡P. The diatomic SiP, **6**, is a σ radical and has a triple bond with a length of 1.993 Å. The SiP triple bond appears to be ca. 40 kcal/mol stronger than the double bond, based on the following isodesmic reactions:

$$SiH_3 + PH_2 + SiH_2{=}PH \rightarrow HSi{\equiv}P + SiH_4 + PH_3 \qquad -35.3 \text{ kcal/mol}$$

$$SiH_3 + PH_2 + SiH{=}PH \rightarrow Si{\equiv}P + SiH_4 + PH_3 \qquad -47.2 \text{ kcal/mol}$$

(f) Si_2PH_7. Disilylphosphine, **7**, has geometrical parameters that are very similar to monosilylphosphine, **1a**. The bond separation energy is small:

$$SiH_3PHSiH_3 + PH_3 \rightarrow 2SiH_3PH_2 \qquad 2.8 \text{ kcal/mol}$$

indicating relatively little interaction between the two Si−P bonds. By comparison with **1b** the corresponding ylide is expected to be 30−40 kcal/mol higher in energy. The SiH_3-SiH_2PH_2 isomer[39] is 4.9 kcal/mol higher than **7**.

(g) Si_2PH_6. Similar to $SiPH_4$, the lowest energy Si_2PH_6 structure, **8a**, is the $^2B_1$ state resulting from breaking a P−H in Si_2PH_7; the $^2A_1$ state is 29.1 kcal/mol higher. Cleavage of an Si−H bond in Si_2PH_7 yields **8b**, a structure that is 8.2 kcal/mol higher than **8a**. This structure is the silyl-substituted analogue of **2b**. The *gauche* rotomer is 0.9 kcal/mol higher than the *anti* rotomer.

(h) Si_2PH_5. Of the structures considered, the phosphorus-bridged, 3-membered-ring **9a** has the lowest energy. The Si−P bond length is slightly longer than an average Si−P single bond (2.280 Å vs 2.25 Å), whereas the Si−Si bond length is intermediate between a single and a double bond (2.264 Å vs 2.335 Å in $H_3Si{-}SiH_3$ and 2.164 Å in $H_2Si{=}SiH_2$[40]). The shortening of Si−Si bonds in $H_2Si{-}X{-}SiH_2$ 3-membered rings (X = PH, S, NH, O) has been attributed to back-donation from X into the $H_2Si{=}SiH_2$ π^* orbital[26a,b] and to bond bending.[26c] Ring strain can be estimated by the following homodesmic reactions:

$$\text{cyclic } SiH_2PHSiH_2 + 2SiH_3PH_2 + SiH_3SiH_3 \rightarrow 2SiH_3SiH_2PH_2 + SiH_3PHSiH_3 \qquad -27.6 \text{ kcal/mol}^{39}$$

$$\text{cyclic } SiH_2SiH_2SiH_2 + 3SiH_3SiH_3 \rightarrow 3SiH_3SiH_2SiH_3 \qquad -33.6 \text{ kcal/mol}$$

$$\text{cyclic } CH_2CH_2CH_2 + 3CH_3CH_3 \rightarrow 3CH_3CH_2CH_3 \qquad -27.4 \text{ kcal/mol}^{39}$$

The ring strain for cyclic Si_3H_6 is higher than that of cyclopropane because of increased bond bending strain and greater difficulty in forming suitable hybrid orbitals at silicon.[26b,c] The decrease in ring strain in going from cyclic Si_3H_6 to cyclic Si_2PH_5 is due to a decrease in angular strain because of the smaller valence angles at phosphorus.[26b] West and co-workers[48] have tentatively identified a substituted example of 3-membered-ring **9a** as an intermediate in the reaction of P_4 with disilenes.

The acyclic compound with a double bond, $SiH_3P{=}SiH_2$ **9b**, is only 2.0 kcal/mol higher than the cyclic structure, **9a**. The π-bond energy is very similar to $SiH_2{=}PH$:

$$SiH_3 + PH_2 + SiH_3{-}PH{-}SiH_3 \rightarrow SiH_3{-}P{=}SiH_2 + SiH_4 + PH_3 \qquad -39.6 \text{ kcal/mol}$$

Driess et al.[18d] have recently synthesized a sterically stabilized $R_2Si{=}P{-}SiR'_3$, where R and R′ are large, bulky groups. They have also compared observed and calculated properties for $R_2Si{=}XR$ and $R_2Si{=}PSiR_3$.[29] The calculated geometry of **9b** is essentially $H_2Si{=}PH$, **3a**, substituted by a silyl group; the structure shows little specific interaction between the Si−P single and double bonds.

The silylene isomer, *anti* SiH_3PHSiH **9c**, and its *syn* conformer are silyl-substituted analogues of **3b** and are 13.8 and 14.9 kcal/mol higher than **9b**. Each of these silylenes has a remarkably small HSiP angle (less than 90°), a 0.02−0.03 Å shortening of both the SiP bonds, and a flattening of the pyramidal P, indicating some interaction between the silyl group and the $H_2Si{=}P$ moiety. This is confirmed by examining the appropriate bond separation reaction:

$$SiH_3PHSiH + PH_3 \rightarrow SiH_3PH_2 + SiHPH_2 \qquad 4.9 \text{ kcal/mol}$$

(i) Si_2PH_4. The lowest energy structure is the $^2B_1$ state of the 3-membered-ring **10a**. It can be obtained by breaking the P−H bond in the 3-membered-ring **9a** and shows even more shortening of the Si−Si bond than the latter. The $^2A_1$ state is a ca. 10 kcal/mol less stable than the $^2B_1$ state. The other 3-membered ring, **10b**, is 7.2 kcal/mol higher than **10a**. The

(47) Colegrove, B. T.; Schaefer, H. F. *J. Phys. Chem.* **1990**, *94*, 5593.
(48) Fanta, A. D.; Tan, R. P.; Comerlato, N. M.; Driess, M.; Powell, D. R.; West, R. *Inorg. Chim. Acta* **1992**, *198−200*, 733.

ring strain in these structures is similar to cyclic Si_2PH_5, **9a**, as computed by the following isodesmic reactions:

$$\text{cyclic } SiH_2PSiH_2 + 2SiH_4 \rightarrow SiH_3PSiH_3 + SiH_3SiH_3 \quad -23.5 \text{ kcal/mol}$$

$$\text{cyclic } SiH_2PHSiH + 2SiH_4 \rightarrow SiH_3PHSiH_2 + SiH_3SiH_3 \quad -22.5 \text{ kcal/mol}$$

$$\text{cyclic } SiH_2PHSiH_2 + 2SiH_4 \rightarrow SiH_3PHSiH_3 + SiH_3SiH_3 \quad -24.6 \text{ kcal/mol}$$

The most stable acylic structure is *trans* $H_3SiPH{=}SiH$, **10c**, which is 6.8 kcal/mol higher than **10a**. The *cis* isomer of $H_3SiPH{=}SiH$ is 2.8 kcal/mol less stable than the *trans*. Structure **10d**, SiH_3PHSi, is 10.9 kcal/mol above **10a** and is the silyl-substituted analogue of H_2PSi, **4a**; both SiP bonds in **10d** show ca. 0.02 Å shortening, indicating some interaction between the bonds:

$$SiH_3PHSi + PH_3 \rightarrow SiH_3PH_2 + SiPH_2 \quad 5.1 \text{ kcal/mol}$$

Breaking the Si−Si bond and opening the 3-membered ring in **10a** is endothermic by only 10.5 kcal/mol (however, there is probably a significant barrier); the resulting species, **10e**, is isoelectronic with allyl radical and the SiP bond lengths are intermediate between single and double bonds. From the following isodesmic reaction,

$$2SiH_3 + PH_2 + SiH_3PHSiH_3 \rightarrow SiH_2PSiH_2 + 2SiH_4 + PH_3 \quad -43.0 \text{ kcal/mol}$$

one can see that the strength of the allylic π bond is slightly greater than π-bond energy of the double bond in $SiH_2{=}PH$. Structures **10f** and its *syn* isomer can be obtained by Si−Si bond cleavage and ring opening of **10b** (endothermic by 16.2 and 18.1 kcal/mol, respectively). In both of these isomers, the P═SiH fragments resemble **3b**, although the P is less pyramidal; the $H_2Si{-}P$ fragments resemble **2b**, but the Si−P bond is somewhat shorter, indicating a small interaction with the neighboring Si═P.

(j) Si_2PH_3. Three different cyclic species can be constructed. Structure **11a** is the most stable and has a somewhat elongated Si−P single bond and Si═P double bond, but an SiSi bond that is almost as short as $H_2Si{=}SiH_2$. The Si═P π-bond energy, as estimated by the following isodesmic reaction,

$$SiH_3 + PH_2 + \text{cyclic } SiH_2{-}PH{-}SiH_2 \rightarrow \text{cyclic } SiH_2{-}P{=}SiH + SiH_4 + PH_3 \quad -40.4 \text{ kcal/mol}$$

is similar to acyclic Si═P double bonds in **3a** and **9b** (−37.9 and −39.6 kcal/mol, respectively). Silylene **11b** is 7.9 kcal/mol higher than **11a** and can be obtained by 1,1-H_2 elimination from **9a**. The SiSi bond is normal, but the SiP bonds are 0.05−0.06 Å shorter than normal. The ring strain in **11b** is somewhat less than in **9a** because of the smaller valence angle of silylenes:

$$\text{cyclic } SiH_2PHSi + 2SiH_4 \rightarrow SiH_3PHSiH + SiH_3SiH_3 \quad -17.8 \text{ kcal/mol}$$

Structure **11c** with an Si═Si double bond is a transition state for PH migration. The acyclic isomer **11d** has an SiP single bond and an SiP double bond. This structure is 16.3 kcal/mol above **11a** and can be generated from **9b** by 1,1-elimination of H_2 to give a silylene or by breaking the SiSi doble bond in **11a**. The geometry of **11d** resembles **3a** substituted with a silylene and there is a sizable interaction between the two SiP bonds:

$$SiH_2{=}P{-}SiH + PH_3 \rightarrow SiH_2{=}PH + SiH{-}PH_2 \quad 7.0 \text{ kcal/mol}$$

Compound *anti*,*anti*-**11e**, the *syn*,*anti* isomer, and the *syn*,*syn* isomer have π systems that are isoelectronic with allyl cation and the Si−P bonds show the requisite shortening. The structures are 25.6, 26.4, and 27.3 kcal/mol above **11a**, respectively.

(k) Si_2PH_2. Isomer **12a** is the most stable and can be obtained from **10a** by 1,1-elimination of H_2 or from **11b** by PH bond cleavage. There is considerable shortening of the SiP bond to give it nearly double bond character. The other two cyclic structures, **12b** and **12c**, are significantly higher in energy (21.0 and 25.2 kcal/mol, respectively). In both cases there is a partial multiple bond in the ring. Acyclic isomers HSiPSiH and HSiPHSi were also considered, but were found to be significantly less stable than the cyclic structures.

(l) Si_2PH and Si_2P. The three-membered ring with an Si−H bond, **13a**, is 11.2 kcal/mol more stable than the isomer with a P−H bond, **13b**. The $^2A_1$ state is the most stable state for Si_2P, **14**; the $^2B_2$ state is 19.8 kcal/mol higher. Structure **13a** has an SiP single bond while **13b** and **14** have SiSi single bonds; the other ring bonds have partial double bond character.

(m) Si_3PH_9. Trisilylphosphine, **15**, is a pyramidal with the silyl groups in a staggered conformation. At the Hartree−Fock level, the symmetry is C_{3v}, but at the MP2/6-31G(d) level the silyl groups twist by ca. 10° to yield an equilibrium structure with C_3 symmetry. Because there are 3 pairs of Si−P bond interactions, the bond separation energy for Si_3PH_9 is approximately 3 times the bond separation energy for Si_2PH_7:

$$(SiH_3)_3P + 2PH_3 \rightarrow 3SiH_3PH_2 \quad 9.8 \text{ kcal/mol}$$

Heats of Formation, Bond Energies, and Decomposition Reactions. The G2 energies (listed in the supporting information) were used to calculate the atomization energies listed in Table 1. These were then combined with the gas-phase heats of formation of the atoms to give the heats of formation of the molecules under discussion. While the heats of formation of hydrogen and phosphorus atoms are known very well[49] (52.10 and 75.62 kcal/mol, respectively, at 298 K, 1 atm), there is a bit of uncertainty for silicon. Grev and Schaefer[50] and Ochterski, Petersson, and Wiberg[51] have recently suggested the value listed in the JANAF tables,[47] 107.55 ± 2 kcal/mol (at 298 K), is too low based on a comparison between very high level calculations and the experimental heat of atomization of silane and disilane. We have used their recommendation[50,51] of 108.1 ± 0.5 kcal/mol at 0 K or 109.1 kcal/mol at 298 K. For a series of 125 energy differences whose experimental values are known accurately, the mean absolute error in the values calculated at the G2 level of theory is 1.3 kcal/mol.[30,31] The accuracy and reliability of calculated heats of formation listed in Table 1 should be similar. For the molecules in the present study, the mean absolute difference in atomization energies computed at the G2 and G2(MP2) levels of theory is 0.5 kcal/mol (G2(MP2) results are available in the supporting information).

Table 2 presents the dissociation enthalpies for the weakest bonds in the compounds considered. Simple Si−H, P−H, and

(49) Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Szverud, A. N. JANAF Thermochemical Tables, 3rd ed. In *J. Phys. Chem. Ref. Data* **1985**, *14*.

(50) Grev, R. S.; Schaefer, H. F. *J. Chem. Phys.* **1992**, *97*, 8389.

(51) Ochterski, J. W.; Petersson, G. A.; Wiberg, K. B. *J. Am. Chem. Soc.* **1995**, *117*, 11299.

Table 1. Atomization Energies, Heats of Formation, and Entropies for $SiPH_n$, Si_2PH_n, and Si_3PH_9 Computed at the G2 Level of Theory[a]

	structure	symmetry	atomization energy	heat of formation	entropy
1a	H_3Si-PH_2	C_s	428.5	9.7	66.1
1b	H_2Si-PH_3	C_s	394.2	44.2	67.6
2a	H_3Si-PH $^2A''$	C_s	347.5	40.0	66.8
2b	H_2Si-PH_2 *anti*	C_s	339.6	47.9	66.9
3a	$H_2Si{=}PH$	C_s	293.5	42.9	62.0
3b	$HSi-PH_2$	C_1	279.2	57.4	63.3
3c	H_3Si-P	C_{3v}	272.1	64.3	62.4
3d	$Si-PH_3$	C_{3v}	247.1	89.5	64.1
4a	H2Si═P	C_s	213.7	72.1	63.0
4b	$HSi{=}PH$ *trans*	C_s	208.8	76.9	62.8
4c	$Si-PH_2$	C_s	204.7	80.9	63.1
5a	Si(H)P	C_s	166.4	68.8	61.6
5b	$HSi{\equiv}P$	$C_{\infty v}$	156.0	79.0	56.0
6	$Si{\equiv}P$	$C_{\infty v}$	83.1	100.8	54.8
7	$H_3Si-PH-SiH_3$	C_s	633.3	15.1	80.2
8a	$H_3Si-P-SiH_3$ $^2B_1$	C_2	552.9	44.8	83.1
8b	$H_3Si-PH-SiH_2$ *anti*	C_1	544.7	53.0	80.9
9a	$H_2Si-PH-SiH_2$ c	C_s	502.0	44.2	71.7
9b	$H_3Si-P{=}SiH_2$	C_s	500.1	46.5	75.5
9c	$H_3Si-PH-SiH$ *anti*	C_1	486.2	60.5	77.4
10a	$H_2Si-P-SiH_2$ c $^2B_1$	C_{2v}	422.7	72.8	72.5
10b	$H_2Si-PH-SiH$ c	C_1	415.6	79.9	72.4
10c	$H_3Si-P{=}SiH$ *trans*	C_s	416.0	80.0	78.1
10d	$H_3Si-PH-Si$	C_1	411.8	84.1	77.5
10e	$H_2Si-P-SiH_2$	C_2	412.2	83.9	77.0
10f	$H_2Si-PH{=}SiH$ *anti*	C_1	399.4	96.7	77.2
11a	$H_2Si-P-SiH$ c	C_s	369.6	74.9	69.2
11b	$H_2Si-PH-Si$ c	C_1	361.8	83.1	71.0
11d	$H_2Si{=}P-SiH$ *anti,anti*	C_s	353.3	91.8	73.3
11e	$HSi-PH-SiH$	C_{2v}	344.1	101.2	77.5
12a	$H_2Si-P-Si$ c	C_s	300.8	93.2	71.4
12b	$HSi-PH-Si$ c	C_1	279.8	114.2	71.3
12c	$HSi-P-SiH$ c	C_2	275.6	118.4	70.9
13a	$HSi-P-Si$ c	C_s	247.4	95.7	67.7
13b	$Si-PH-Si$ c	C_{2v}	236.2	107.0	69.2
14	$Si-P-Si$ c $^2A_1$	C_{2v}	183.1	109.2	67.1
15	$(SiH_3)_3P$	C_3	842.5	16.5	92.5

[a] G2 atomization energies in kcal/mol at 0 K, heats of formation in kcal/mol at 298 K, entropies in cal/deg mol at 298 K; cyclic molecules are designated by the suffic c.

Table 2. Energies for Unimolecular Decomposition Computed at the G2 Level of Theory[a]

	structure	bond breaking[b]				elimination	
		SiH	PH	SiP	SiSi	H_2	SiH_2
1a	H_3Si-PH_2	88.9	81.0	70.1		45.0	54.9
1b	H_2SiPH_3		54.6	20.7		−3.5	
2a	H_3Si-PH	54.0	75.4	64.8		34.5	55.5
2b	H_2Si-PH_2	60.4	46.1	47.6		21.7	
3a	$H_2Si{=}PH$	84.7	79.8	77.2 (100.6)			22.9
3b	$HSi-PH_2$	74.6	70.4	63.6		19.0	
3c	H_3Si-P	58.5		58.6			55.9
3d	$Si-PH_3$		42.5	20.7			
4a	H2Si═P	57.7		66.6 (89.9)		26.3	
4b	$HSi{=}PH$	42.4	52.8	68.9			
4c	$Si-PH_2$		38.2	59.8		17.3	
5a	Si(H)P		83.3	97.3			
5b	$HSi{\equiv}P$	72.9		85.3 (126.6)			
6	$Si{\equiv}P$			83.1			
7	$H_3Si-PH-SiH_3$	88.6	80.4	72.3		42.9	57.7
8a	$H_3Si-P-SiH_3$	52.8		67.2		32.7	59.1
8b	$H_3Si-PH-SiH_2$	42.7	44.6	37.6		42.5	58.0
9a	$H_2Si-PH-SiH_2$ c	86.5	80.4		15.8	36.1	61.4
9b	$H_3Si-P{=}SiH_2$	84.1		72.9		42.6	59.4
9c	$H_3Si-PH-SiH$	74.4	70.3	63.9		38.0	59.9
9d	$H_3Si-PH-SiH$	73.4	69.2	62.9		36.9	58.8
10a	$H_2Si-P-SiH_2$ c	53.1			6.8	17.7	61.9
10b	$H_2Si-PH-SiH$ c	53.8	45.9		17.6	31.5	59.6
10c	$H_3Si-P{=}SiH$	62.6		46.4			60.0
10d	$H_3Si-PH-Si$	50.1		31.9			60.0
10e	$H_2Si-P-SiH_2$	58.9		51.4			
10f	$H_2Si-PH{=}SiH$	55.3	46.0	43.4			
11a	$H_2Si-P-SiH$ c	68.8			16.3	18.0	66.5
11b	$H_2Si-PH-Si$ c	81.9	60.9			21.3	48.2
11d	$H_2Si{=}P-SiH$	52.5		68.9			
11e	$HSi-PH-SiH$	64.3	68.5	64.5			
12a	$H_2Si-P-Si$ c	53.4				32.7	70.6
12b	$HSi-PH-Si$ c	43.6	32.4				
12c	$HSi-P-SiH$ c	28.2					
13a	$HSi-P-Si$ c	83.5					
13b	$Si-PH-Si$ c		72.3				
15	$(SiH_3)_3P$			76.0			62.0

[a] In kcal/mol at 0 K for breaking the weakest bond; cyclic molecules are designated by the suffix c. [b] Values in parentheses are calculated using triplet SiH_2 and quartet SiH; these are appropriate for determining the SiP double and triple bond strength.[42]

Si−P bond cleavage in saturated compounds requires 70−90 kcal/mol. The strength of an Si═P double bond, 77−80 kcal/mol, is only about 10% greater than a normal single bond strength, 70−76 kcal/mol, based on singlet silylene as a product. If one uses triplet SiH_2,[42] the Si═P double bond is ca. 30 kcal/mol stronger than the single bond. Likewise, if quartet SiH is used, the SiP triple bond is ca. 50−60 kcal/mol stronger than the single bond. Lower values for bond strengths in some of the compounds are due to unstable reactants or particularly stable products. For example, Si−H breaking in **2a**, **8a**, and **10a** and P−H breaking in **2b**, **8b**, and **10b** are 45−55 kcal/mol because of the formation of an Si═P double bond. Formation of silylenes also leads to low Si−H bond energies in **2b**, **4a**, **8b**, and **10e**. The Si−P bond energies in **1b**, **3d**, and **10d** are only 20−32 kcal/mol because the reactants are relatively unstable. Note, however, that there may be significant barriers associated with some of the bond-breaking processes that involve rearrangement of bonding.

Other important routes for the decomposition of silicon compounds are the 1,1-elimination of H_2 and silylene-elimination reactions. The heats of reaction for some of these processes that can be computed from the present data are also listed in Table 2. Of the reactions listed, only $SiH_3PH_2 \rightarrow SiH_2 + PH_3$ and $SiH_3PH_2 \rightarrow SiHPH_2 + H_2$ have been studied previously.[24,25] Typically, silylene insertions and additions have very low barriers. Hence, the barriers for H_2 and SiH_2 elimination will be only a bit higher than the heats of reaction listed in the table (by contrast, 1,2-elimination of H_2 can have rather high barriers[52]). Some of the more facile decomposition reactions include H_2 elimination from **2b**, **3a**, **3b**, **4d**, **10a**, **11a**, and **11b**. In each case the product is stabilized by the formation of a multiple bond. The heats of reaction for SiH_2 elimination are typically 10−20 kcal/mol higher than 1,1-elimination of H_2.

A bond additivity scheme[53] can be constructed to fit the calculated atomization energies in Table 1 and related data for SiH_n, Si_2H_n, Si_3H_8,[41] and PH_n. Because of the special nature of their bonding, ylides H_2SiPH_3 and $SiPH_3$ and partial aromatic 3-membered rings **13a**, **13b**, and **14** were not included. Note that the average bond energies used for the additivity scheme are not the same as the dissociation energies (kcal/mol) for specific bonds in individual compounds:

Si−H = 73.5	P−H = 73	
Si−Si = 55	Si═Si = 57	Si≡Si = 71
Si−P = 55	Si═P = 69	Si≡P = 86
3-membered ring = −30		

These average bond energies yield an estimated mean absolute deviation of 5.3 kcal/mol in the atomization energies. The major

(52) Gordon, M. S.; Truong, T. N.; Bonderson, E. K. *J. Am. Chem. Soc.* **1986**, *108*, 1421.
(53) Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419.

errors in the bond additivity scheme are due to the stability of silylenes, dative bonding, and conjugation. The ring strain term was needed for a reasonable fit, but further refinement is probably not warranted for the size of the database.

A group additivity scheme[53] can give a significantly better fit to the atomization energy:

92 kcal/mol for Si with 4 single bonds
68 kcal/mol for Si with 1 double bond and 2 single bonds
56 kcal/mol for Si with 1 triple bond and 1 single bond
56 kcal/mol for Si with 3 single bonds
44 kcal/mol for Si with 1 double bond and 1 single bond
37 kcal/mol for Si with 1 triple bond
41 kcal/mol for singlet Si with 2 single bonds
17 kcal/mol for triplet Si with 2 single bonds
37 kcal/mol for Si with 1 double bond
17 kcal/mol for Si with 1 single bond
72 kcal/mol for P with 3 or 4 single bonds
65 kcal/mol for P with 1 double bond and 1 single bond
46 kcal/mol for P with 1 triple bond
43 kcal/mol for P with 2 single bonds or 1 double bond
18 kcal/mol for triplet P with 1 single bond
53.3 kcal/mol for terminal H, 60 kcal/mol for bridging H
−14 kcal/mol for 3-membered rings
14 kcal/mol for each dative bond
35 kcal/mol for allylic π conjugation in an Si−P−Si group

For 18 compounds in the series for SiH_n, Si_2H_n, and Si_3H_8 the mean absolute deviation is 1.3 kcal/mol in the atomization energies. For the entire set of $SiPH_n$, Si_2PH_n, Si_3PH_9, SiH_n, Si_2H_n, Si_3H_8, and PH_n (58 compounds), the mean absolute deviation is 3.4 kcal/mol. Special terms for ring strain, dative bonding (e.g structures **3b**, **4c**, **9c**, **10d**, **10f**, etc)., and allylic conjugation (structures **10e**, **11e**, **12c**, **13a**, **13b**, and **14**) were required for a good fit. This scheme should to be a useful start for approximating the energies of larger systems. As more data become available, the group contributions will need to be extended to a larger set of groups with more specific bonding.

Another method for estimating the energies involves isodesmic reactions (reactions that conserve the numbers of each type of bond). For example, the atomization energies of acyclic Si_2PH_n can be approximated from the energies of $SiPH_n$ using the reaction:

$$SiH_mPH_a + SiH_nPH_b \rightarrow SiH_mPH_{3-a-b}SiH_n + PH_3$$

For perfect additivity of bond energies, the reaction enthalpy would be zero. For 12 acyclic Si_2PH_n, the average reaction energy is 5.7 kcal/mol, indicating a significant 1,3-interaction. The average deviation, however, is only 1.7 kcal/mol indicating that the 1,3-interaction is fairly constant and that the estimated energies are much less variable than the bond or group additivity methods. Furthermore, isodesmic reaction energies can be computed quite reliably at fairly low levels of theory (e.g. MP2/6-31G(d)). Thus, the $SiPH_n$ and Si_2PH_n energies in the present work can be used as templates to estimate the energies of larger systems using isodesmic reactions.

Summary

The present study examined a total of 48 isomers and states of silicon−phosphorus compounds at the G2 level of theory. There are a number of examples of Si−P double bonds. Silylenes and cyclic compounds are also abundant for structures with low numbers of hydrogens. Some of these are stabilized by dative bonding and allylic conjugation. Structure **9b** is the parent of a sterically stabilized compound synthesized by Driess.[18] Compounds based on 3-membered-ring **9a** and possibly silylene **9c** are also interesting candidates for synthesis because of their structure and stability. Other molecules that might be considered include unsaturated rings, **11a** and **11b**, and species with allylic conjugation, **11e** and **10e**. The calculated heats of formation provide a guide to the relative energies and stabilities of the various isomers. Simple bond additivity and group additivity schemes have been developed for estimating the energies of larger systems.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE 9400678). We would like to thank the Pittsburgh Supercomputing Center for computer time.

Supporting Information Available: Total energies at the MP2(full)/6-31G(d), QCISD(T)/6-311G(d,p), G2(MP2), and G2 levels of theory, and harmonic vibrational frequencies at the HF/6-31G(d) level for all structures (4 pages). See any current masthead page for ordering and Internet access instructions.

JA960771W