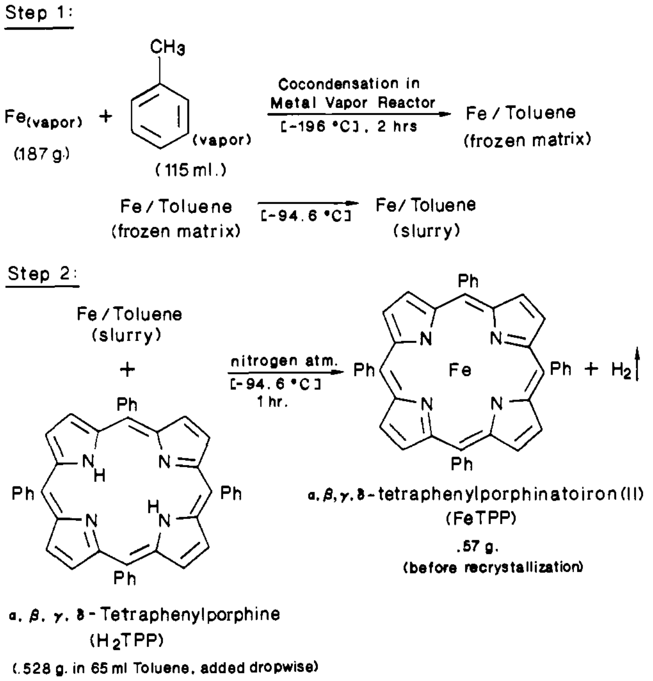
Scheme I



slurry. In step 2, a saturated solution (65 mL) of H_2TPP in toluene is added dropwise to the low-temperature (−94.6 °C) slurry. After addition of the H_2TPP to the slurry, the mixture is reevacuated and allowed to gradually warm to 0 °C. Upon warming, the evolution of gas is observed, indicating facile reactivity at the *N*-hydrogen of the H_2TPP. Filtration of the cold product mixture through a fine porosity frit removes unreacted metal and any insoluble material, resulting in a highly pure reaction product of the metalloporphyrin in toluene. After solvent removal, characterization of the solid reaction product using mass spectrometry, UV–vis spectroscopy, and infrared spectroscopy showed FeTPP, a trace of its oxygen degradation product, and no residual H_2TPP.

Mass spectrum (70 eV, 300 °C) showed 91 *m/e* as the base peak from residual toluene and a strong molecular ion peak at 668 *m/e* corresponding to FeTPP. No peak at 614 *m/e* corresponding to H_2TPP was detected. Except for a trace of its oxygen degradation product, the UV–vis spectrum in benzene showed a nearly clean spectrum of Fe/TPP with characteristic bands[6] at 419, 443, and 539 nm. No evidence for unreacted free H_2TPP was observed.

The overall reaction resulted in essentially 100% conversion of the H_2TPP used resulting in 0.57 grams (before recrystallization) of the ferrous porphyrin. The reaction requires an excess of iron in order to ensure the complete conversion of H_2TPP to FeTPP. We used a 4:1 molar ratio to ensure an excess of "reactive" metal, as metal agglomeration can be a competing process. The entire reaction can be completed in less than 5 h via this synthetic route. Advantages of this synthetic route vs. those previously reported[7] include a short reaction time, inexpensive reagents (H_2TPP and Fe metal), and a clean reaction yielding the ferrous porphyrin in quantitative yield.

Using cobalt in Scheme I has resulted in a low-yield synthesis (<2%) of CoTPP while nickel does not produce any detectable NiTPP. In metal atom reactions of pyrrole with the first row group VIII transition metals we have found the following general trend of reactivity: Fe $\gg$ Co > Ni (no reaction). Accordingly, α,β,γ,δ-tetraphenylporphine reactions with iron, cobalt, and nickel parallel the pyrrole reactivity pattern. It seems likely that the iron reactivity can be extended to a variety of porphyrins, phthalocyanines, polypyrrole, and other macrocycles incorporating the pyrrole functionality. Indeed, preliminary results using indole in a reaction analogous to the porphyrin reaction reported here has resulted in a reactive but stable iron/indole product. Exploration of this metalation reaction at the *N*-hydrogen of pyrrole and the pyrrole functionality with other transition metals on a preparative scale similar to that of iron is under investigation.

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Why Are π Bonds to Phosphorus More Stable toward Addition Reactions than π Bonds to Silicon?

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A clear example of the significant difference in stability toward addition reactions between compounds containing doubly-bonded silicon ($=SiR_2$)[1] and doubly-bonded phosphorus ($=PR$)[2] is found in the comparison of silabenzenes[3] with phosphabenzenes.[4] The former compounds dimerize so rapidly that they can only be isolated in inert matrices at very low temperatures.[5] In contrast, phosphabenzenes are perfectly stable toward dimerization at ambient temperatures and only react with hexafluoro-2-butyne, a potent Diels–Alder dienophile, on heating to 100 °C.[6]

In this communication we report the results of ab initio calculations, which show that π bonds in phosphenes are, in fact, substantially more thermodynamically stable toward addition reactions than π bonds in silenes. We show that two factors contribute to this difference—π bonds in phosphenes are stronger than π bonds in silenes, and σ bonds in silanes are stronger than σ bonds in phosphines. Both of these factors can be traced to the preference in the second row of the periodic table for orbitals containing unshared electrons to have large amounts of s character.

The calculations reported here were all performed with the 3-21G$^{(*)}$ basis set.[7] Geometries were optimized with RHF wave functions for closed-shell species[8] and with UHF wave functions for radicals. Electron correlation was included by using second-order Møller–Plesset (MP2) perturbation theory.[9,10] All calculations were carried out with GAUSSIAN 82.[12]

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[10] The MP2 energies of $CH_2{=}SiH_2$ and $CH_3{-}SiH_3$ and the UHF and MP2 energy of CH_3SiH_2 were published[11] while our study was in progress.

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Table I. 3-21G$^{(*)}$ RHF/UHF and MP2 Energies for the Molecules in Eq 1–3

molecule	RHF/UHF energy[a]	MP2 energy[a]
$CH_2{=}SiH_2$	−327.3921[b]	−327.5665[c]
$CH_3\text{–}SiH_2$	−328.0028[c]	−328.1619[c]
$CH_3\text{–}SiH_2$[d]	−327.9865	−328.1492
$CH_3\text{–}SiH_3$	−328.6227[b]	−328.7953[c]
$CH_2{=}PH$	−378.4463[b]	−378.6421
$CH_3\text{–}PH$	−379.0446	−379.2224
$CH_3\text{–}PH_2$	−379.6411[b]	−379.8336

[a] RHF for closed-shell molecules, UHF for radicals, energies in hartrees. [b] Geometry and RHF energy from ref 8. [c] Energy from ref 11. [d] Geometry optimized with Si constrained to be planar.

Equation 1 represents a hydrogen-transfer reaction from methylphosphine to silene, affording phosphene and methylsilane.

$$CH_3\text{–}PH_2 + CH_2{=}SiH_2 \rightarrow CH_2{=}PH + CH_3\text{–}SiH_3 \quad (1)$$

From the energies given in Table I, eq 1 is computed to be exothermic by 22.5 kcal/mol at the RHF level and 21.5 kcal/mol at the MP2 level of theory. The substantial exothermicity that is calculated for this reaction indicates that at least part of the experimental difference in stability toward addition reactions between C=Si and C=P π bonds[1-4] has a thermodynamic origin.

In order to assess the contribution of the relative strengths of the C=Si and C=P π bonds to the exothermicity of the reaction in eq 1, we calculated the difference in the energies liberated by the addition of a hydrogen atom to carbon in both phosphene and silene. Since eq 2 measures the difference between the relative energies of the doubly-bonded compounds and those of the $CH_3\text{–}X^\bullet$ radicals formed from them, this energy difference can be taken as a measure of the relative π bond strengths of silene and phosphene. Our UHF/RHF calculations give 7.8 kcal/mol as the exothermicity of the reaction in eq 2; the MP2 value is 9.5 kcal/mol.[13]

$$CH_3\text{–}PH^\bullet + CH_2{=}SiH_2 \rightarrow CH_2{=}PH + CH_3\text{–}SiH_2^\bullet \quad (2)$$

We have previously argued that the pyramidal geometry which is favored for silyl radicals weakens the π bonds in silenes.[14] Maximal π overlap requires doubly-bonded silicon to adopt a planar geometry, but, when the π bond to silicon is broken, the silyl radical that is formed pyramidalizes, releasing energy. However, pyramidalization is undefined for dicoordinate phosphorous; so this effect does not weaken the π bonds in phosphenes.

The contribution of silyl radical pyramidalization to the energy calculated for eq 2 can be assessed by reoptimizing the geometry of the methylsilyl radical with the silicon constrained to be planar. The geometry thus optimized is calculated to be 10.2 kcal/mol (UHF) and 7.9 kcal/mol (MP2) higher in energy than the unconstrained geometry in which silicon is allowed to pyramidalize.[15] These calculations indicate that silyl radical pyramidalization accounts for nearly all of the computed difference between the energy of the π bonds in silene and phosphene.

However, the energy difference between these two π bonds in eq 2 comprises only between 35% (UHF/RHF) and 44% (MP2) of that computed for eq 1. The remainder of the difference between the energy of hydrogen addition to phosphene and to silene is due to the energy of eq 3, which is computed to be exothermic by between 14.7 kcal/mol (RHF/UHF) and 12.0 kcal/mol (MP2).

$$CH_3\text{–}PH_2 + CH_3\text{–}SiH_2^\bullet \rightarrow CH_3\text{–}PH^\bullet + CH_3\text{–}SiH_3 \quad (3)$$

The exothermicity calculated for this reaction is indicative of a substantially greater strength for an Si–H bond in methylsilane than for a P–H bond in methylphosphine. The difference between the experimental bond dissociation energy of silane (90.3–98.0 kcal/mol)[18] and that of phosphine (82.5–85.1 kcal/mol)[19] is consistent with this theoretical result.[20]

Because the bond dissociation energies in AH_n increase monotonically across the first row of the periodic table from CH_4 to HF,[21] the decrease in going from SiH_4 to PH_3 in the second row is at first surprising. However, this difference, like that between carbon- and silicon-centered radicals in their tendency to pyramidalize, can be understood as a consequence of the fact that in the second row of the periodic table orbitals for unshared electrons tend to have much larger amounts of s character than such orbitals in the first row.[14,22]

As a result, whereas the bond angles in NH_3 and H_2O are each well in excess of 100°, thus indicating the idealized hybridization of these bonds approaches the nominal sp^3 hybridization of CH_4, the bond angles in PH_3 and H_2S are each close to 90°, thus suggesting that orbitals with much less s character are utilized for these latter bonds. However, unlike PH_3 or H_2S, SiH_4 is without lone pairs of electrons. Therefore, SiH_4, like CH_4, adopts a tetrahedral geometry and forms Si–H bonds from orbitals that are nominally sp^3 hybrids. Consequently, on going from SiH_4 to PH_3, there is a significantly larger decrease in the amount of s character in the bonds to hydrogen than on going from CH_4 to NH_3.[22]

Since decreasing the amount of s character in a bond decreases the strength of that bond,[23] we attribute the drop in bond dissociation energy on going from SiH_4 to PH_3 to the difference between the hybridization of the bonds in these compounds. The greater strength of an Si–H bond in silanes, compared to a P–H bond in phosphines, is responsible for a major part (56–65%) of the calculated difference between phosphene and silene in thermodynamic stability toward hydrogen addition.

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Supplementary Material Available: UHF 3-21G$^{(*)}$ optimized geometry of CH_3PH and of CH_3SiH_2 with the geometry at silicon constrained to be planar (1 page). Ordering information is given on any current masthead page.

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(20) The calculated difference between the bond dissociation energy of SiH_4 and that of PH_3 is 12.8 kcal/mol with RHF/UHF and 10.3 kcal/mol with MP2. It should be noted, however, that, unless very large basis sets are used, ab initio calculations, which include electron correlation, underestimate the bond dissociation energy of ammonia by 2–3 kcal/mol more than that of methane [Pople, J. A.; Frisch, M. J.; Luke, B. T.; Binkley, J. S. *Int. J. Quantum Chem., Symp.* **1983**, *17*, 307]. This fact suggests that the calculations reported here probably tend to overestimate slightly the difference between the bond dissociation energies of silanes and phosphines.

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(23) A familiar example is the decrease in the C–H bond dissociation energy along the series ethyne > ethene > ethane.[21]