What Accounts for the Remarkable Difference between Silabenzene and Phosphabenzene in Stability toward Dimerization?

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B3LYP/6-31G* calculations have been performed in order to understand the tremendous difference between silabenzene and phosphabenzene in stability toward dimerization. The calculations find that dimerization is exothermic by $\Delta H = -21.5$ kcal/mol for silabenzene but endothermic by $\Delta H = 32.6$ kcal/mol for phosphabenzene. The difference of 54.1 kcal/mol between these enthalpies of dimerization is reproduced to within 11% by twice the difference between the heats of H_2 addition across one of the π bonds between carbon and the heteroatom in each molecule. This finding allows the H_2 addition reactions to be used to analyze the origins of the huge difference between the heats of dimerization. The calculations show that the energy of a π bond to the heteroatom is smaller in silabenzene than in phosphabenzene, but this difference accounts for less than 20% of the difference between the heats of H_2 addition. The major factor is the much greater strength of the σ bond formed to silicon than to phosphorus, and additional calculations have allowed the three contributors to this large difference in σ bond strengths to be identified.

A striking example of the difference in reactivities between compounds containing Si−C[1] and P−C[2] π bonds[3] is provided by the comparison between silabenzene and phosphabenzene. For example, silabenzenes dimerize at very low temperatures,[4] although bulky substituents can be used to inhibit[5] or prevent[6] these bimolecular Diels−Alder reactions. In contrast, phosphabenzene[7] is very unreactive toward cycloaddition. It does not dimerize, and it only undergoes a Diels−Alder reaction with hexafluoro-2-butyne after 2 days of heating at 100 °C.[8]

The development of density functional theory (DFT) has made it practical to perform accurate calculations on the dimerization of phosphabenzene and silabenzene and, hence, to explore the causes of the striking difference in reactivities between these two molecules. Herein, we report the results of B3LYP/6-31G* calculations which find that this difference in reactivity has a thermodynamic origin. Our calculations also show the major cause of the very large difference in calculated heats of dimerization is not the difference between the strengths of the Si−C and P−C π bonds in the reactants that are broken but, instead, the difference between the strengths of the σ bonds to silicon and to phosphorus that are formed in the products.

Computational Methodology

All calculations were carried out with the Gaussian 98 suite of programs[9] using the 6-31G* basis set.[10] Geometry optimizations were performed utilizing Becke's hybrid three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP).[11] A vibrational analysis was

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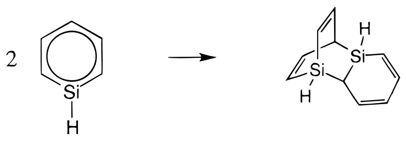
performed at each stationary point found, to confirm its identity as an energy minimum or a transition structure. The harmonic frequencies were used, without scaling, to calculate the zero-point energies and thermal corrections necessary to obtain the enthalpies of reaction. Optimized geometries, energies, and enthalpies of all the molecules discussed in this paper can be found as Supporting Information.

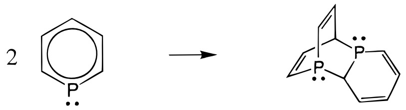
Results and Discussion

Dimerization Reactions. We began by calculating the enthalpy of Diels–Alder dimerization of 2 mol of each heterobenzene. This reaction is shown in eq 1 for silabenzene (SB) and in eq 2 for phosphabenzene (PB). The enthalpy computed for each reaction is given under the equation for it.



(1)

ΔH = -21.5 kcal/mol

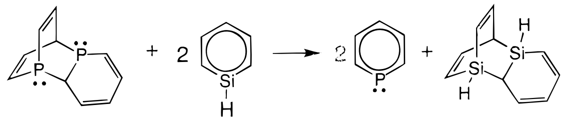


(2)

ΔH = 32.6 kcal/mol

As expected, the dimerization of SB was computed to be highly exothermic. In contrast, the dimerization of PB was calculated to be even more highly endothermic. Thus, the reason that the dimerization of PB is not observed is quite simple—thermodynamically, this reaction is very unfavorable.

The isodesmic reaction in eq 3 represents the difference between the heats of dimerization of SB and PB, and it is, therefore, extremely exothermic. An obvious question is whether the considerable exothermicity of the reaction in eq 3 is due primarily to a difference between the strengths of the Si–C and P–C π bonds in the reactants, which are broken in the dimerization reactions, or to a difference between the strengths of the Si–C and P–C σ bonds that are formed in the Diels–Alder dimerization products.

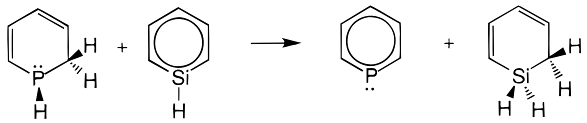


(3)

ΔH = -54.1 kcal/mol

To answer this question most conveniently, we chose to model the formation of the Si–C and P–C bonds in eqs 1 and 2 with the Si–H, P–H, and C–H bonds formed when H_2 is added to a π bond between carbon and the heteroatom in SB and in PB. For this model to be valid, the difference between the heats of H_2 addition to 2 mol each of SB and PB must be comparable to the difference between the heats of dimerization of SB and PB.

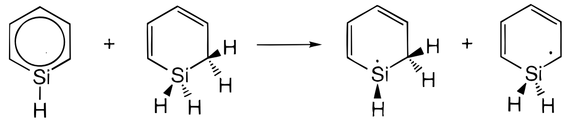
The difference between the heats of dimerization of SB and PB is given by twice the enthalpy of the isodesmic reaction in eq 4.[12] Twice the enthalpy of this reaction is 48.0 kcal/mol. This value differs by only 11% from the value of $\Delta H = -54.1$ kcal/mol for the reaction in eq 3. Therefore, determining the origins of the difference between the heats of H_2 addition to SB and PB provides not only a tractable but also a reasonable way to try to understand the reasons for the very large difference between their heats of dimerization.



(4)

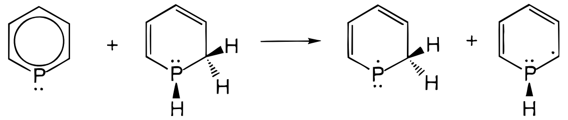
ΔH = - 24.0 kcal/mol

Relative π Bond Strengths. Perhaps the most obvious of the possible sources of the 24.0 kcal/mol difference between the heats of H_2 addition to an Si=C bond in SB and to a P=C bond in PB is that the former type of π bond is much weaker than the latter. Employing Benson's definition of π bond strengths,[13] we computed the Si–C and P–C π bond dissociation enthalpies in SB and PB as the enthalpies of the isodesmic reactions in, respectively, eqs 5 and 6. The calculated value of $DH^{298}\pi$(Si–C) is only 2.6 kcal/mol smaller than that of $DH^{298}\pi$(P–C). Therefore, the difference in Benson π bond dissociation enthalpies contributes only about 10% of the difference between the heats of H_2 addition to an Si=C bond in SB and a P=C bond in PB.



(5)

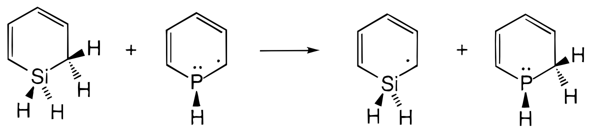
$DH^{298}\pi$(Si-C) = 34.8 kcal/mol



(6)

$DH^{298}\pi$(P-C) = 37.4 kcal/mol

Another possible contributor to the calculated difference between the heats of H_2 addition to SB and PB is the difference between the strengths of the C–H bonds formed. This difference is given by the enthalpy of the isodesmic reaction in eq 7.



(7)

ΔH = 1.9 kcal/mol

Presumably, because stabilization of the 6-phosphacyclohexadienyl radical by the lone pair on the phosphorus atom is slightly larger than the stabilization of the 6-silacyclohexadienyl radical by hyperconjugation

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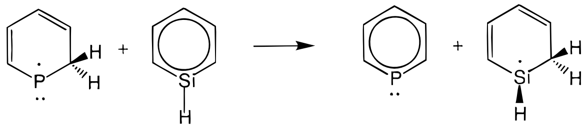
[12] The exothermicity calculated for the reaction in eq 4 is about 10 times larger than the value of $\Delta H = -2.5$ kcal/mol computed for the analogous isodesmic reaction that gives the difference between the heats of H_2 addition to the first-period congeners pyridine and benzene.

[13] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

with the Si−H bonds, the C−H bond formed upon addition of H_2 to PB is calculated to be slightly weaker than the C−H bond formed upon addition of H_2 to SB. The results of both experiments and high quality ab initio calculations are consistent with this B3LYP finding. Brauman and co-workers have compared the experimental C−H bond dissociation enthalpies (BDEs) of $(CH_3)_4Si$ and $(CH_3)_3P$ and found that a C−H bond is stronger by ca. 3 kcal/mol in tetramethylsilane than in trimethylphosphine.[14] G2 calculations by Wiberg and Nakaji have found a similar difference between the C−H BDEs of CH_3SiH_3 and CH_3PH_2.[3c]

Stabilization of the 6-phosphacyclohexadienyl radical by the lone pair on the phosphorus atom also weakens the P−C π bond in PB, relative to the Si−C π bond in SB. However, the difference between heterocyclohexadienyl radical stabilization energies cancels if the difference between the strengths of the C−H bonds formed upon addition of H_2 to SB and PB (which is given by the isodesmic reaction in eq 7) is subtracted from the difference between the strengths of the π bonds broken (which is given by the difference between the enthalpies of the reactions in eqs 5 and 6). Subtracting eqs 6 and 7 from eq 5 produces the isodesmic reaction in eq 8.



(8)

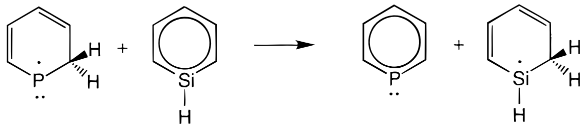
ΔH = - 4.5 kcal/mol

This isodesmic reaction gives the difference between the enthalpies of adding a hydrogen atom to an *ortho* carbon of SB and of PB. This enthalpy difference is equal to $\Delta H = -2.6 - 1.9 = -4.5$ kcal/mol. It seems reasonable to assume that, without selective stabilization of the cyclohexadienyl radical by the phosphorus lone pair, the strengths of the C−H bonds formed in the addition of H_2 to SB and PB would be exactly the same. If this assumption is made, then 4.5 kcal/mol represents the difference between the *intrinsic* strengths of the Si−C and P−C π bonds in SB and PB, when the selective weakening of the latter from radical stabilization by the phosphorus lone pair is ignored.

Why is the Si−C π Bond Weaker than the C−P π Bond? We have previously shown that pyramidalization of radical centers weakens the π bonds formed to them.[3b,15] Silyl radical centers prefer pyramidal geometries,[16] and, as in 1-silaallyl radical,[15d] conjugation with the adjacent double bond does not supply a driving force sufficient to induce the 1-sila-2,4-cyclohexadienyl radical in eq 8 to adopt a planar geometry. Consequently, pyramidalization of this silyl radical weakens the Si−C π bond in SB, in which the silicon has a planar geometry.

In contrast, the two-coordinate phosphoryl radical center in 1-phospha-2,4-cyclohexadienyl radical is necessarily planar. Therefore, pyramidalization of this center obviously does not weaken the P−C π bond in PB. Consequently, silyl radical pyramidalization weakens the π bond in SB, relative to the π bond in PB.

The amount of energy by which the π bond in SB is weakened by the preference of the 1-sila-2,4-cyclohexadienyl radical in eq 8 for a pyramidalized geometry can easily be obtained by computing the amount of energy required to constrain the silyl radical center to planarity. Decreasing the angle between the Si−H bond and the C−Si−C plane from its equilibrium value of 48.7° to 0° is calculated to increase the enthalpy of the 1-sila-2,4-cyclohexadienyl radical by 4.2 kcal/mol. Thus, the isodesmic reaction in eq 9, in which the silyl radical center in eq 8 is constrained to be planar, is almost thermoneutral.



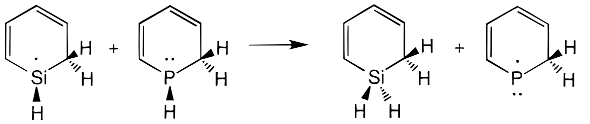
(9)

ΔH = - 0.3 kcal/mol

If the reaction in eq 8 is taken to provide the best measure of the difference between the intrinsic strengths of the Si−C and P−C π bonds in, respectively, SB and PB, then the isodesmic reaction in eq 9 provides the same information about the intrinsic strengths of these π bonds when both of the 1-hetero-2,4-cyclohexadienyl radicals in this equation are planar. Therefore, the near-zero enthalpy that is computed for the isodesmic reaction in eq 9 shows that the Si−C π bond in SB and the P−C π bond in PB would have almost exactly the same strength, if it were not for the 4.2 kcal/mol preference of the silyl radical center in 1-sila-2,4-cyclohexadienyl radical for a pyramidal geometry.

Difference Between Si−H and P−H σ Bond Strengths. The reaction in eq 8 gives the sum of the differences between the strengths of the π bonds broken plus the C−H σ bonds made upon addition of a hydrogen atom to an α-carbon of SB and PB. The sum of these two differences amounts to only 4.5 kcal/mol. Therefore, the remainder of the 24.0 kcal/mol difference between the heats of H_2 addition to SB and PB must be due to a 19.5 kcal/mol difference between the strengths of the Si−H and P−H bonds formed in these reactions.

It is easy to demonstrate that this is, indeed, the case. Subtracting eq 8 from eq 4 gives eq 10. The enthalpy of



(10)

ΔH = -19.5 kcal/mol

$\Delta H = -19.5$ kcal/mol for the isodesmic reaction in eq 10 is equal to the difference between the BDEs of the P−H bond in 1-phospha-2,4-cyclohexadiene and the Si−H bond in 1-sila-2,4-cyclohexadiene. The much greater strength of the Si−H bond, formed in the addition of H_2 to SB, than the P−H bond, formed in the addition of H_2 to PB, is responsible for more than 80%

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(14) Römer, B.; Gatev, G. G.; Zhong, M.; Brauman, J. I. *J. Am. Chem. Soc.* **1998**, *120*, 2919.

(15) See, *inter alia*: (a) Cherry, W.; Epiotis, N. D.; Borden, W. T. *Acc. Chem. Res.* **1977**, *10*, 167. (b) Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1985**, *107*, 2596. (c) Coolidge, M. B.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 1704. (d) Coolidge, M. B.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 2354. (e) Johnson, W. T. G.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 5930. (f) Review: Borden, W. T. *Chem. Commun.* **1998**, 1919.

(16) (a) Sakurai, H.; Murakami, M. *J. Am. Chem. Soc.* **1969**, *91*, 519. (b) Brook, A. G.; Duff, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 2119. (c) Krusic, P. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1969**, *91*, 3938.

Table 1. Calculated and Experimental Bond Dissociation Enthalpies (DH^{298}) in kcal/mol

bond	DH^{298}		
	B3LYP/6-31G*	G2	expt
H_3Si-H	90.0	92.7[a]	91.7[b]
$MeSiH_2-H$	90.6	93.7[c]	92.2[d]
Me_2SiH-H	91.4		
Me_3Si-H	92.1		95.1[e]
H_2P-H	79.9	82.9[f]	83.9,[b] 80.9[g]
$MePH-H$	78.1	81.9[h]	74.4–79.0[i]
Me_2P-H	76.8		

[a] Reference 3c gives $DH^0 = 91.3$ kcal/mol. [b] From ref 19. [c] Reference 3c gives $DH^0 = 92.3$ kcal/mol. [d] From ref 24b. [e] From ref 23. [f] Reference 3c gives $DH^0 = 81.5$ kcal/mol. [g] From ref 20. [h] Ref 3c gives $DH^0 = 80.5$ kcal/mol. [i] From ref 26.

of the 24.0 kcal/mol difference between the enthalpies of these two reactions.

Contribution of Hybridization to the Difference between Si−H and P−H BDEs. Since in the first row of the periodic table C−H bonds are, in general, weaker than N−H bonds,[17] the 19.5 kcal/mol greater strength of the Si−H bond in 1-sila-2,4-cyclohexadiene than the P−H bond in 1-phospha-2,4-cyclohexadiene might seem surprising. However, we have previously pointed out that the much greater amount of 3s character in the bonds formed by tetravalent silicon than by trivalent phosphorus[18] makes Si−H bonds in silanes stronger than P−H bonds in phosphines.[3b] For example, as shown in Table 1, B3LYP/6-31G* computes the difference between $DH^{298}(H_3Si-H) = 90.0$ kcal/mol and $DH^{298}(H_2P-H) = 79.9$ kcal/mol to be 10.1 kcal/mol.

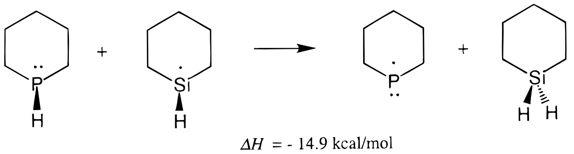
As also shown in Table 1, an experimental value in the range $DH^{298}(H_3Si-H) = 91.7 \pm 0.5$ kcal/mol has been deduced for H_3Si-H.[19] The two experimental values of $DH^{298}(H_2P-H) = 83.9$[19] and 80.9 kcal/mol[20] that have most recently been recommended for H_2P-H span a much wider range. The average of these two values, $DH^{298}(H_2P-H) = 82.4$ kcal/mol, differs from the value $DH^{298}(H_3Si-H) = 91.7$ kcal/mol by 9.3 kcal/mol. This difference is slightly smaller than the B3LYP/6-31G* difference of $DH^{298}(H_3Si-H) - DH^{298}(H_2P-H) = 10.1$ kcal/mol.

Another way of evaluating the accuracy of the B3LYP/6-31G* value for the difference between the H_3Si-H and H_2P-H BDEs is to compare this value with that computed by a very high quality ab initio method. For example, as shown in Table 1, G2 calculations[21] give $DH^{298}(H_3Si-H) = 92.7$ kcal/mol and $DH^{298}(H_2P-H) = 82.9$ kcal/mol. The value of 9.8 kcal/mol for the difference between the H_3Si-H and H_2P-H BDEs, computed at this level of ab initio theory, is very close to the B3LYP/6-31G* value of 10.1 kcal/mol.

If the difference in hybridization between silicon in 1-sila-2,4-cyclohexadiene and phosphorus in 1-phospha-2,4-cyclohexadiene contributes 10.1 kcal/mol to the B3LYP/6-31G* exothermicity of $\Delta H = -19.7$ kcal/mol for the isodesmic reaction in eq 10, nearly half of the exothermicity of this reaction remains unaccounted for. What other factors contribute to the difference between the Si−H and P−H BDEs, which is given by the enthalpy of this reaction?

Contribution of Alkyl Substituents to the Difference between Si−H and P−H BDEs. The radical centers in eq 10 are both secondary. Therefore, rather than comparing the B3LYP/6-31G* BDEs of H_3Si-H and H_2P-H, a better comparison for the reaction in eq 10 would be the difference between the B3LYP/6-31G* BDEs of $(CH_3)_2SiH-H$ and $(CH_3)_2P-H$. As shown in Table 1, the B3LYP/6-31G* difference between the BDEs of $(CH_3)_2SiH-H$ and $(CH_3)_2P-H$ is computed to be 14.6 kcal/mol. This difference is 4.5 kcal/mol larger than the B3LYP/6-31G* difference between the BDEs of H_3Si-H and H_2P-H.

An even more appropriate comparison for the isodesmic reaction in eq 10 is the isodesmic reaction in eq 11, which gives the difference between the P−H BDE in phosphacyclohexane and the Si−H BDE in silacyclohexane. The B3LYP/6-31G* enthalpy of $\Delta H = -14.9$ kcal/mol for this reaction demonstrates that the difference between the secondary P−H and Si−H bond strengths is nearly the same between phosphacyclohexane and silacyclohexane as between dimethylphosphine and dimethylsilane.



(11)

As shown in Table 1, there is experimental evidence that, as predicted by B3LYP/6-31G*, G2,[3c] and other ab initio[22a] and DFT[22b] calculations, the Si−H BDE really does increase with increasing methyl substitution on silicon.[23,24] The increase in Si−H BDEs with increasing alkyl substitution can be attributed to the fact that, because silyl radical centers are pyramidal, hyperconjugative stabilization of silyl radicals is negligible. Since carbon is slightly more electronegative than hydrogen and since, in the absence of other effects, electronegative substituents tend to increase BDEs,[25] the small increase in Si−H BDEs with increasing alkyl substitution can be understood.[22a]

Since, in contrast to the case with silyl radical centers, phosphoryl radical centers are necessarily planar, phosphoryl radicals can be better stabilized by hyperconjugation than silyl radicals. As shown in

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(17) For a glaring exception to this generalization and a discussion see: Kemnitz, C. R.; Karney, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1998**, *120*, 3499.

(18) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

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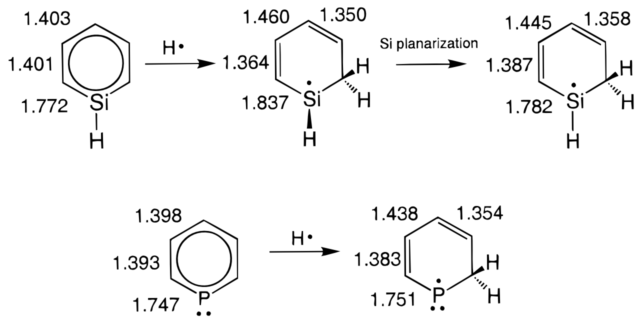


Figure 1. Changes in the B3LYP/6-31G* bond lengths (Å) that occur upon addition of a hydrogen atom to SB and PB and upon planarization of silicon in the radical formed from SB.

Table 1, alkyl substituents are, in fact, computed to lower P−H BDEs. As also shown in Table 1, there is experimental evidence that, as predicted, P−H BDEs do decrease with increasing substitution on phosphorus.[26]

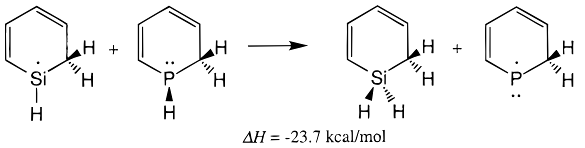
The increase in Si−H BDEs and the decrease in P−H BDEs with increasing alkyl substitution is responsible for the computational finding that the B3LYP difference between the Si−H and P−H BDEs, given by the enthalpy of the isodesmic reaction in eq 11, is 4.8 kcal/mol larger than the B3LYP difference between the BDEs of H_3Si-H and H_2P-H. Nevertheless, the value of $\Delta H = -14.9$ kcal/mol for the isodesmic reaction in eq 11 is still 4.6 kcal/mol smaller in size than $\Delta H = -19.5$ kcal/mol for the isodesmic reaction in eq 10.

Contribution of Adjacent Double Bonds to the Difference between Si−H and P−H BDEs. Equations 10 and 11 differ in that the double bonds, present in the compounds in eq 10, are absent from the compounds in eq 11. The presence of the double bonds obviously increases the difference between the Si−H and P−H BDEs by 4.6 kcal/mol. The question is why the double bonds have this effect.

One possible answer to this question is that, as already noted, the phosphoryl radical center in 1-phospha-2,4-cyclohexadienyl radical is necessarily planar, whereas the silyl radical center in 1-sila-2,4-cyclohexadienyl radical is pyramidal, with an angle of 48.7° between the Si−H bond and the C−Si−C plane. Therefore, the unpaired electron in 1-phospha-2,4-cyclohexadienyl radical is more delocalized by the adjacent double bonds than the unpaired electron in 1-sila-2,4-cyclohexadienyl radical. The difference in delocalization between these two radicals is manifested in the difference between the bond lengths in them, which are given in Figure 1.

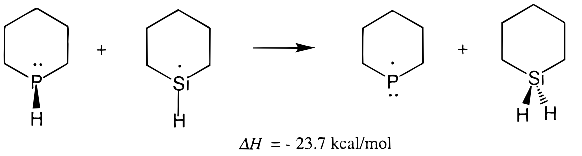
To establish whether the pyramidal geometry of the 1-sila-2,4-cyclohexadienyl radical really is the major contributor to the 4.6 kcal/mol difference between the isodesmic reactions in eqs 10 and 11, it is useful to consider variants of these two reactions in which the Si radical center in each reaction is constrained to be planar. Constraining the silyl radical center in 1-sila-2,4-cyclohexadienyl to planarity should make the delocalization of the unpaired electron in this radical much closer to that in 1-phospha-2,4-cyclohexadienyl radical. That this is, in fact, the case is indicated by the similarity of the bond lengths in these two radicals, which are also given in Figure 1.

As already noted, constraining the 1-sila-2,4-cyclohexadienyl radical on the left-hand side of eq 10 to planarity is computed to require 4.2 kcal/mol. Consequently, the exothermicity of the isodesmic reaction in eq 12, in which the silyl radical center is thus constrained, is $\Delta H = -19.5 - 4.2 = -23.7$ kcal/mol.



(12)

By also planarizing the silyl radical center in 1-silacyclohexyl, as in eq 13, the contribution of the double bonds in the compounds in eq 12 to the exothermicity of the isodesmic reaction in this equation can be obtained. Inversion of the silyl radical center in 1-silacyclohexyl radical is computed to require 8.8 kcal/mol at the B3LYP/6-31G* level. The 4.6 kcal/mol lower barrier to inversion, computed for 1-sila-2,4-cyclohexadienyl radical, is the amount by which conjugation with the double bonds reduces the barrier to planarizing the silyl center in the latter radical.



(13)

When the effect of the 8.8 kcal/mol increase in energy on planarization of the radical center in 1-silacyclohexyl is added to $\Delta H = -14.9$ kcal/mol for eq 11, eq 13 is computed to be exothermic by $\Delta H = -23.7$ kcal/mol. Thus, the enthalpy of the isodesmic reaction in eq 13 is computed to be exactly the same as that of the isodesmic reaction in eq 12. This result shows that the presence of the two double bonds in the compounds in eq 10 has no effect on the difference between the Si−H and P−H BDEs in eq 11, *provided* that the silyl radical centers in both these equations are constrained to be planar, as they are in eqs 12 and 13.

The identical enthalpies of eqs 12 and 13 imply that the π bonds formed to the planarized silyl radical center in 1-sila-2,4-cyclohexadienyl and to the phosphoryl radical center in 1-phospha-2,4-cyclohexadienyl have essentially the same strength, provided that the π conjugation energies of 1-phospha- and 1-sila-2,4-cyclohexadiene are the same. The enthalpy of the isodesmic reaction in eq 14 shows that the heats of hydrogenation of the two dienes are computed differ by only 0.4 kcal/mol, thus indicating that the π conjugation energies of these two dienes are, in fact, nearly the same.[27]

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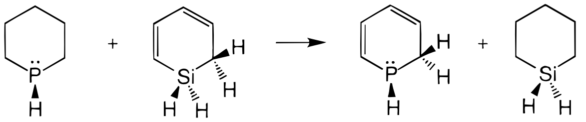
[26] Berger, S.; Brauman, J. I. *J. Am. Chem. Soc.* **1992**, *114*, 4737.

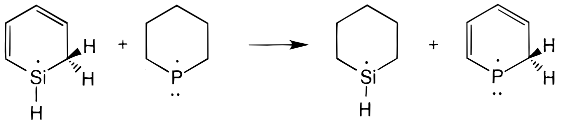
[27] This finding is not very surprising, since comparison of the angles between the P−H bond and the C−P−C plane in 1-phospha-2,4-cyclohexadiene (78.2°) and in phosphacyclohexane (77.9°) indicates that there is little conjugation between the lone pair of electrons on phosphorus and the double bonds in 1-phospha-2,4-cyclohexadiene. The P−C bond to the unsaturated carbon in 1-phospha-2,4-cyclohexadiene is 0.038 Å shorter than the P−C bond to the saturated carbon. However, most of this difference is almost certainly due to the difference in hybridization between these two carbons, rather than to P−C π bonding, since the two Si−C bond lengths in 1-sila-2,4-cyclohexadiene actually differ by slightly more, 0.041 Å.



(14)

ΔH = - 0.4 kcal/mol

Subtraction of eq 13 from eq 12 and addition of eq 14 then yields eq 15. The small enthalpy of the isodesmic reaction in eq 15 confirms that the π systems of planar 1-sila-2,4-cyclohexadienyl radical and 1-phospha-2,4-cyclohexadienyl radical really do have nearly the same energies, since the heats of hydrogenation of the double bonds in these radicals are computed to differ by only 0.4 kcal/mol. Finally, the near-thermoneutrality of the reaction in eq 9 ($\Delta H = -0.3$ kcal/mol), which involves these planar radicals, implies that the delocalized π systems of SB and PB are also nearly isoenergetic, with that of PB being the lower in energy, but only by 0.7 kcal/mol.



(15)

ΔH = - 0.4 kcal/mol

Contribution of Pyramidalization to the Difference between Si−H and P−H BDEs. Equation 15 shows that the π bond to silicon in the *planar* 1-sila-2,4-cyclohexadienyl radical has nearly the same strength as the π bond to phosphorus in the 1-phospha-2,4-cyclohexadienyl radical. However, as already noted, the pyramidal silyl radical center at the equilibrium geometry of 1-sila-2,4-cyclohexadienyl radical actually makes the C−Si π bond in this radical weaker than the C−P π bond in 1-phospha-2,4-cyclohexadienyl radical. In fact, our calculations find this difference between the C−Si and C−P π bond strengths (or, equivalently, between the delocalization energies of the unpaired electrons on the heteroatoms) in 1-sila-2,4-cyclohexadienyl and 1-phospha-2,4-cyclohexadienyl radicals to be almost wholly responsible for the 4.6 kcal/mol difference between the isodesmic reactions in eqs 10 and 11.

Despite the presence of the double bonds in 1-sila-2,4-cyclohexadienyl radical, the angle between the C−Si−C plane of 48.7° is actually rather close to that (51.9°) in 1-silacyclohexyl radical. Nevertheless, the barrier to inversion of the radical center in the former radical is computed to be only 4.2 kcal/mol, compared to 8.8 kcal/mol in the latter radical. The greater delocalization of 1-sila-2,4-cyclohexadienyl radical at the planar geometry for inversion of the silyl radical center compared to that at the equilibrium geometry of this radical is clearly responsible for the lowering of the barrier to silyl radical inversion by the adjacent double bonds.

Therefore, a good estimate of the difference between the delocalization energies at the planar and at the equilibrium geometries of 1-sila-2,4-cyclohexadienyl radical is provided by the difference of $8.8 - 4.2 = 4.6$ kcal/mol between the barriers to silyl radical inversion in the 1-silacyclohexyl and the 1-sila-2,4-cyclohexadienyl radicals. Thus, the pyramidal equilibrium geometry of the 1-sila-2,4-cyclohexadienyl radical puts it at a 4.6 kcal/mol disadvantage with respect to the necessarily planar 1-phospha-2,4-cyclohexadienyl radical, and this difference fully accounts for the 4.6 kcal/mol difference between the energies of the isodesmic reactions in eqs 10 and 11.[28] This difference is the third and final contributor to the 19.5 kcal/mol difference between the Si−H BDE in 1-sila-2,4-cyclohexadiene and the P−H BDE in 1-phospha-2,4-cyclohexadiene.

Conclusions

In finding that the dimerization of SB is exothermic by $\Delta H = -21.5$ kcal/mol and that of PB is endothermic by $\Delta H = 32.6$ kcal/mol, the results of our B3LYP/6-31G* calculations are consistent with the huge difference observed between the reactivity of these two compounds toward dimerization. The fact that the difference between the heats of dimerization is only about 11% larger than twice the calculated difference of 24.0 kcal/mol between the heats of H_2 addition to SB and PB indicates that the hydrogenation reactions can serve as good models for the dimerization reactions.

We have used the difference between the addition of H_2 to an Si−C π bond in SB and to a P−C π bond in PB to try to understand the difference between the reactivities toward dimerization of these two heterobenzenes. Our calculations reveal that the intrinsic strengths of an Si−C π bond in SB and a P−C π bond in PB are not very different. The difference of 4.5 kcal/mol, given by the enthalpy of the isodesmic reaction in eq 8, is less than 20% of the difference between the computed heats of H_2 addition to SB and PB. The near-thermoneutrality of eq 9, in which the silyl radical in eq 8 is constrained to be planar, shows that the weaker π bond in SB can almost entirely be attributed to the preference of the silyl radical center for a pyramidal geometry.

Our B3LYP/6-31G* calculations indicate that 19.5 kcal/mol of the difference between the enthalpies of the H_2 addition reactions to SB and PB resides in the difference between the strengths of the Si−H and P−H bonds that are formed. Of this 19.5 kcal/mol, a little over half comes from the larger amount of 3s character in the bonds formed by tetravalent silicon than in the bonds formed by trivalent phosphorus. The 10.1 kcal/mol difference between the H_3Si-H and the H_2P-H B3LYP/6-31G* BDEs is attributed to this difference in hybridization.

A calculated contribution of an additional 4.8 kcal/mol to the difference between the strengths of the Si−H bond formed in the addition of H_2 to SB and the P−H bond formed in the addition of H_2 to PB comes from the fact that alkyl substitution strengthens bonds to silicon but weakens bonds to phosphorus. Hyperconjugation provides less stabilization for silyl radicals, which are pyramidal, than for phosphoryl radicals, which are necessarily planar; this effect acts to make the difference between Si−H and P−H BDEs increase with increasing alkyl substitution.

The source of the remaining 4.6 kcal/mol difference between the strengths of the bonds, formed at each of the heteroatoms in the addition of H_2 to SB and PB, is

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[28] The 0.4 kcal/mol stabilizing interaction between the phosphorus lone pair and the adjacent double bond in 1-phospha-2,4-cyclohexadiene (eq 14) is, fortuitously, exactly canceled in eq 10 by the 0.4 kcal/mol greater delocalization energy of 1-phospha-2,4-cyclohexadienyl radical, relative to planar 1-sila-2,4-cyclohexadienyl radical (eq 15).

also related to the difference between the geometries of silyl and phosphoryl radicals. Our calculations find that the difference in delocalization energies, caused by the difference between the pyramidal equilibrium geometry of the 1-sila-2,4-cyclohexadienyl radical and the necessarily planar geometry of the 1-phospha-2,4-cyclohexadienyl radical, contributes 4.6 kcal/mol to the difference between the Si−H BDE in 1-sila-2,4-cyclohexadiene and the P−H BDE in 1-phospha-2,4-cyclohexadiene.

An important general point is illustrated by the results of our calculations of the relative heats of H_2 addition to SB and PB. Although it may be tempting to attribute a difference in reactivities between two compounds to the relative strengths of the bonds broken when each reacts, it is often the case that the major contributor is, instead, the relative strengths of the bonds that are formed.[29] From the results of our calculations on the addition of H_2 to SB and PB, we conclude it is the difference in strengths between the bonds made to silicon in the dimerization SB and to phosphorus in the dimerization of PB that is chiefly responsible for making dimerization exothermic for SB but highly endothermic for PB.

Acknowledgment is made to the National Science Foundation for support of this research. The calculations reported here were performed on an IBM RS/6000 computer cluster, whose purchase was also made possible by a grant from the National Science Foundation.

Supporting Information Available: Figures and tables giving optimized geometries and B3LYP/6-31G* energies for all the molecules that appear in eqs 1−12. This material is available free of charge via the Internet at http://pubs.acs.org.

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[29] See, for example: (a) Nicolaides, A.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 6750. (b) Hrovat, D. A.; Duncan, J. A.; Borden, W. T. *J. Am. Chem. Soc.* **1999**, *121*, 169. (c) Reference 15e.