Heats of Formation of Diphosphene, Phosphinophosphinidene, Diphosphine, and Their Methyl Derivatives, and Mechanism of the Borane-Assisted Hydrogen Release

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The heats of formation of diphosphene (*cis-* and *trans-*P_2H_2), phopshinophosphinidene (singlet and triplet H_2PP) and diphosphine (P_2H_4), as well as those of the P_2H and P_2H_3 radicals resulting from PH bond cleavages, have been calculated by using high-level ab initio electronic structure theory. Energies were calculated using coupled-cluster theory with a perturbative treatment for triple excitations (CCSD(T)) and employing augmented correlation consistent basis sets with additional tight d-functions on P (aug-cc-pV(n+d)Z) up to quadruple- or quintuple-ζ, to perform a complete basis set extrapolation for the energy. Geometries and vibrational frequencies were determined with the CCSD(T) method. Core-valence and scalar relativistic corrections were included, as well as scaled zero-point energies. We find the following heats of formation (kcal/mol) at 298 [0] K: $\Delta H_f^\circ(P_2H) = 53.4\ [54.4]$; $\Delta H_f^\circ(cis\text{-}P_2H_2) = 32.0\ [33.9]$; $\Delta H_f^\circ(trans\text{-}P_2H_2) = 28.7\ [30.6]$; $\Delta H_f^\circ(H_2PP) = 53.7\ [55.6]$; $\Delta H_f^\circ(^3H_2PP) = 56.5\ [58.3]$; $\Delta H_f^\circ(P_2H_3) = 32.3\ [34.8]$; $\Delta H_f^\circ(P_2H_4) = 5.7\ [9.1]$ (expt, 5.0 ± 1.0 at 298 K); and $\Delta H_f^\circ(CH_3PH_2) = -5.0\ [-1.4]$. We estimate these values to have an accuracy of ± 1.0 kcal/mol. In contrast to earlier results, we found a singlet ground state for phosphinophosphinidene (H_2PP) with a singlet–triplet energy gap of 2.8 kcal/mol. We calculated the heats of formation of the methylated derivatives CH_3PPH, CH_3HPPH_2, CH_3PPCH_3, CH_3HPP, $(CH_3)_2PP$, $(CH_3)_2PPH_2$, and $CH_3HPPHCH_3$ by using isodesmic reactions at the MP2/CBS level. The calculated results for the hydrogenation reactions $RPPR + H_2 \rightarrow RHPPHR$ and $R_2PP + H_2 \rightarrow R_2PPH_2$ show that substitution of an organic substituent for H improves the energetics, suggesting that secondary diphosphines and diphosphenes are potential candidates for use in a chemical hydrogen storage system. A comparison with the nitrogen analogues is given. The mechanism for H_2-generation from diphosphine without and with BH_3 as a catalyst was examined. Including tunneling corrections, the rate constant for the catalyzed reaction is 4.5×10^{15} times faster than the uncatalyzed result starting from separated catalyst and PH_2PH_2.

Introduction

Hydrogen is currently being considered as a promising energy transfer agent, which is friendly to the environment, for the transportation sector.[1] For this to be a viable technology, molecular hydrogen must be stored in a safe, efficient, and sustainable fashion. Considerable efforts are underway to design compounds that can be used in chemical hydrogen storage systems either as such or as reactive intermediates. Not only is the thermodynamics for hydrogen and release important, but also the kinetics of release are important, so there is a search for efficient catalysts for hydrogen release, for example, from amine boranes.[2] We have been exploring the thermodynamics of various types of compounds using high-level ab initio molecular orbital theory to predict accurate heats of formation of relevant compounds. For example, we have studied borane amines[3] as well as related isoelectronic species containing P and Al,[4] stable heterocyclic carbenes,[5] and organic derivatives of diimide (N_2H_2) and hydrazine (N_2H_4)[6] as potential hydrogen storage systems. A necessary condition for a compound ABH_2 to be considered as a H_2 source is that the relevant reaction (1) be near thermoneutral:

$$AB + H_2 \rightarrow ABH_2 \qquad (1)$$
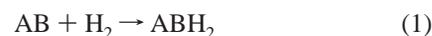
Thus, we need to predict the energetics for the AB and ABH_2 species which in turn enable us to predict the reaction thermodynamics for the addition and loss of a hydrogen molecule. In addition, we have been studying possible catalytic dehydrogenation routes and recently discovered that the borane molecule (BH_3) can act as an efficient bifunctional catalyst facilitating the H_2 release from ammonia borane.[7] In the current work, we extend these studies to diphosphenes and diphosphines, the phosphorus analogues of diimides and hydrazines, respectively.

Although diphosphine (H_2PPH_2), having a single P–P bond, has been known since 1844 and is a prototype of open-chain phosphorus hydrides,[8] the parent diphosphene (HPPH) bearing a double P=P bond has not been extensively studied until recently. The preparation of the first stable diphosphene was reported in 1981 by Yoshifuji and co-workers,[9] who used sterically bulky substituents (RP=PR, R = 2,4,6-tri-*tert*-butylphenyl) to achieve kinetic stability. Since then, the chemistry of this class of low-coordinated P-compounds has rapidly been developed, and they are versatile ligands in transition metal chemistry.[10] More recently, the *meta*-terphenyl

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groups (2,6-Ar$_2$C$_6$H$_3$−) have been shown to be equally effective in providing the steric shielding necessary for stable diphosphenes.[11]

Although in the simplest form, the phosphinophosphinidene isomer (H$_2$PP) is predicted to have a triplet ground state,[12−14] Fritz et al.[15] showed that bulky alkyl-substituted derivatives such as (*tert*-But)$_2$PP can be synthesized and trapped in a closed-shell singlet state. Upon hydrogenation, both singlet diphosphene and phosphinophosphinidene yield isomeric diphosphines as shown in reactions 2 and 3.

$$RP{=}PR + H_2 \rightarrow RHP{-}PRH \quad (2)$$

$$R_2P{=}P + H_2 \rightarrow R_2P{-}PH_2 \quad (3)$$
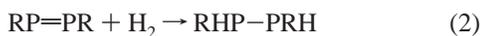
The first goal of the current study is to reliably predict the heats of formation of the parent P$_2$H$_n$ compounds and then use these results to evaluate the ΔH_f°'s of larger organic derivatives on the basis of isodesmic reactions. We have used a composite ab initio molecular orbital theory approach without empirical parameters except for the spin−orbit energies in atoms and the zero-point energies.[16,17] The total atomization energy (TAE) of a molecular system is calculated and used to obtain its heat of formation at 0 K utilizing the known heats of formation of the atoms. The TAE is calculated by using coupled-cluster theory, including a perturbative treatment of the triple excitations (CCSD(T))[18,19] combined with augmented correlation-consistent basis sets[20,21] (including tight d-functions for the P atom), extrapolated to the complete basis set (CBS) limit to treat the correlation energy of the valence electrons. Additional smaller corrections, such as core-valence interactions, relativistic and spin−orbit effects, and the zero-point energies (ZPE), obtained either from a combination of experiment and theory or from theoretical scaled values, are also included. The standard heats of formation of compounds at 298 K can then be calculated by using standard thermodynamic and statistical mechanics expressions.[22]

We used such an approach to calculate the heats of formation of the neutral P$_2$H$_n$ and CH$_3$PH$_2$ species. For the purpose of calibration, the corresponding parameters of the simpler PH$_n$ species were also obtained. Subsequently, we calculated the heats of formation of the substituted compounds RPPH, RPPR, RHPPHR and RRPPH$_2$ for R = CH$_3$ by using an isodesmic reaction approach employing the electronic energies obtained at the second-order perturbation theory and extrapolated to the basis set limit (MP2/CBS). These calculations were based on geometries optimized by using density functional theory level[23] with the B3LYP exchange-correlation functional.[24] This follows the same method as in our previous work on the corresponding nitrogen analogues.[6] The calculated values were then used to assess the hydrogenation energy of reactions 2 and 3 for R = CH$_3$. We predicted the energy barrier for H$_2$-elimination from P$_2$H$_4$ and studied the reaction processes in which the Lewis acid BH$_3$ acts as a catalyst for H$_2$-elimination. Finally, we analyzed the kinetics of both catalyzed and noncatalyzed processes.

Computational Approach

The augmented correlation consistent basis sets aug-cc-pVnZ (n = D, T, Q) were used for the calculations, and for brevity, the basis set names are shortened to aVnZ. Only the spherical components (5d, 7f, and 9g) of the Cartesian one-electron functions were used. Due to the presence of second-row atoms, a set of tight d-functions was also added to the basis of P atoms, giving the aV(n+d)Z basis.[25] For the diatomic PH and P$_2$

molecules, calculations using the larger aV(5+d)Z basis set were also carried out. All of the current computational work was performed with the Gaussian03[26] and MOLPRO-2006[27] programs.

We first describe the calculations for the CCSD(T)/CBS extrapolations. The geometries were optimized at the frozen-core CCSD(T) level with both aVTZ and aV(T+d)Z basis sets. The former level was also employed for the prediction of the harmonic vibrational frequencies of the PH$_n$ (n = 2−3), P$_2$H$_m$ (m = 1−4), and CH$_3$PH$_2$ species, except for the P$_2$H$_3$ radical where the aVDZ basis set was used. The geometry of the BH$_3$-PH$_2$PH$_2$ complex was calculated at the MP2/aV(T+d)Z level as were the frequencies.

For PH$_3$, the calculated harmonic vibrational frequencies were averaged with the corresponding experimental fundamentals to determine the ZPE correction.[28,29] We predict a scaled ZPE of 14.60 kcal/mol for PH$_3$, which is identical to that reported by Leroy et al.,[30] and within 0.2 kcal/mol of the value of 14.79 kcal/mol by Haworth and Bacskay derived from B3LYP frequencies.[31] For PH$_2$, there are just estimated experimental fundamentals,[32] so its ZPE was scaled by a factor of 0.9849 obtained from the ratio of the averaged ZPE of PH$_3$ with the calculated CCSD(T)/aVTZ value.

For the diatomic species, PH and P$_2$, harmonic frequencies and anharmonic constants were calculated from a fifth-order fit[33] of the potential energy curves at the CCSD(T)/aV(Q+d)Z level. The ZPE was calculated by including the anharmonic constant. For PH we obtained a harmonic frequency of 2367.7 cm^{-1} with a respective anharmonic constant of 43.7 cm^{-1}. The corresponding experimental values[34] of 2365.2 and 44.5 cm^{-1} are in excellent agreement with our calculated values. For P$_2$ we obtained 782.7 and 2.7 cm^{-1}; the harmonic value is in excellent agreement with the experimental value of 780.8 cm^{-1}.[35]

For the molecules with two phosphorus atoms and one or more hydrogens, as well as the BH$_3$PH$_2$PH$_2$ complex, the ZPE's were scaled by a factor of 0.9837, obtained from the ratio of the averaged value of CCSD(T)/aVTZ harmonic frequencies and experimental fundamentals[36] with the CCSD(T)/aVTZ value for P$_2$H$_4$. For CH$_3$PH$_2$, the experimental values[37] were averaged with calculated results to obtain its ZPE. For the missing experimental value (see Table 1) we used the corresponding calculated value.

For each molecule, the CCSD(T)/aV(D+d)Z and aV(T+d)Z optimized total energies and the aV(Q+d)Z single-point energy at the CCSD(T)/aV(T+d)Z optimized geometry were extrapolated to the CBS limit using a mixed exponential/Gaussian function of the form

$$E(n) = E_{CBS} + A \exp[-(n-1)] + B \exp[-(n-1)^2] \quad (4)$$

with n = 2, 3, and 4, as proposed by Peterson et al.[38] We used CCSD(T)/aV(n+d)Z single-point calculations at the MP2/aV-(T+d)Z optimized geometry for the BH$_3$PH$_2$PH$_2$ complex in the extrapolation.

To determine the CBS energies from the aV(Q+d)Z and aV-(5+d)Z results, the extrapolation function (5) was used in which l_{max}[39] equals the highest angular momentum present in the basis

$$E(l_{max}) = E_{CBS} + B/l_{max}^3 \quad (5)$$

set. The CCSD(T) calculations for open-shell atoms and molecules were carried out at the R/UCCSD(T) level. In this approach, a restricted open shell Hartree−Fock (ROHF) cal-

TABLE 1: CCSD(T)/aVTZ and CCSD(T)/aV(T+d)Z Optimized Geometries and Vibrational Frequencies

molecule	parameter	geometry[a] aVTZ	aV(T+d)Z	aV(Q+d)Z	symmetry	vibrational frequencies aVTZ[b]	aV(Q+d)Z fitting	expt[c]
PH ($^3\Sigma^-$)	P−H	1.429	1.426	1.424	σ	2353.10[d]	2367.66[d]	2365.20
						43.66[e]	43.74[e]	
PH$_2$ (^{2}B$_1$)	P−H	1.424	1.421		a$_1$	1123.93		[1020.00]
	∠HPH	91.8	91.8		a$_1$	2382.70		[2322.00]
					b$_2$	2391.86		[2327.00]
PH$_3$ (^{1}A$_1$)	P−H	1.419	1.417		a$_1$	1009.17		992
	∠HPH	93.5	93.5		e	1139.78		1118
					e	1139.78		1118
					a$_1$	2406.19		2323
					e	2415.23		2328
					e	2415.23		2328
P$_2$ ($^1\Sigma_g^+$)	P−P	1.916	1.910	1.902	σ_g	771.92[d]	782.65[d]	780.80
						2.75[e]	2.74[e]	
HP=P (^{2}A′)	P−P	2.027	2.020		a′	598.81		
	P−H	1.432	1.429		a′	657.14		
	∠HPP	97.4	96.8		a′	2296.83		
trans-P$_2$H$_2$ (^{1}A$_g$)	P−P	2.051	2.044		a$_g$	599.24		
	P−H	1.426	1.423		b$_u$	671.97		
	∠HPP	93.9	93.9		a$_u$	756.84		
					a$_g$	959.41		
					a$_g$	2353.98		
					b$_u$	2369.98		
cis-P$_2$H$_2$ (^{1}A$_1$)	P−P	2.061	2.055		a$_1$	585.95		
	P−H	1.424	1.421		a$_2$	678.94		
	∠HPP	98.6	98.7		a$_1$	738.65		
					b$_2$	836.71		
					b$_2$	2359.59		
					a$_1$	2383.78		
H$_2$P=P (^{1}A$_1$)	P−P	1.961	1.952		b$_1$	386.14		
	P−H	1.412	1.409		a$_1$	623.84		
	∠HPP	128.6	128.7		b$_2$	675.91		
					a$_1$	1158.70		
					a$_1$	2411.31		
					b$_2$	2411.55		
H$_2$P−P (^{3}A″)	P−P	2.209	2.200		a′	435.89		
	P−H	1.422	1.419		a′	636.38		
	∠HPP	96.5	96.7		a″	669.99		
	∠HPPH	95.0	95.1		a′	1079.36		
					a′	2375.95		
					a″	2387.53		
P$_2$H$_3$ (^{2}A)	P−P	2.244	2.197		a	270.57		
	P−H	1.440	1.422		a	420.33		
	P−H^1	1.433	1.415		a	616.60		
	P−H^2	1.435	1.417		a	628.93		
	∠HPP	91.8	91.9		a	884.17		
	∠H^{1}PP	95.9	96.5		a	1096.39		
	∠H^{2}PP	97.8	98.9		a	2353.05		
	∠H^{1}PPH	157.6	157.4		a	2373.76		
	∠H^{2}PPH	62.0	61.0		a	2399.75		
P$_2$H$_4$ (^{1}A)	P−P	2.238	2.231		a	204.03		216
	P−H	1.419	1.416		a	437.79		438
	P−H	1.419	1.416		b	621.10		613
	∠HPP	99.3	99.4		a	645.37		629
	∠HPP	94.4	94.5		b	810.34		884
	∠HPPH	94.7	94.8		a	879.70		898
	∠HPPH	−17.0	−17.1		b	1110.46		1040
	∠HPPH	77.7	77.7		a	1118.54		1056
					b	2398.20		2283
					a	2403.81		2283
					a	2413.57		2308
					b	2417.36		2308
CH$_3$PH$_z$ (^{1}A′)	C−P	1.867	1.863		a″	240.20		207
	C−H	1.089	1.090		a′	682.32		677
	∠HCP	113.1	113.2		a″	699.19		-
	C−H	1.092	1.092		a′	737.62		740
	∠HCP	108.6	108.6		a′	995.66		977
	∠HCPH	121.5	121.5		a″	1039.78		1017
	P−H	1.420	1.418		a′	1117.72		1086
	∠HPC	97.6	97.6		a′	1328.98		1238
	∠HPCH	47.2	47.2		a′	1485.00		1450
					a″	1490.96		1450

ΔH_f of Diphosphene, Phosphinophosphinidene, and Diphosphine

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TABLE 1: Continued

molecule	parameter	geometry[a]			symmetry	vibrational frequencies		
		aVTZ	aV(T+d)Z	aV(Q+d)Z		aVTZ[b]	aV(Q+d)Z fitting	expt[c]
CH$_3$PH$_2$ (^{1}A') (cont'd)					a''	2393.42		2297
					a'	2400.02		2312
					a'	3043.32		2938
					a''	3124.49		2992
					a'	3138.71		3000
BH$_3$PH$_2$PH$_2$[f]	B–P1		1.931		a	126.52		
	P1–P2		2.192		a	144.64		
	∠BP1P2		112.4		a	183.64		
	B–H1		1.205		a	375.16		
	B–H2		1.203		a	463.86		
	B–H3		1.206		a	564.81		
	∠H1BP1		103.0		a	604.27		
	∠H2BP1		105.1		a	611.64		
	∠H3BP1		102.2		a	795.86		
	∠H1BP1P2		−55.3		a	822.16		
	∠H2BP1P2		−176.2		a	891.03		
	∠H3BP1P2		63.4		a	926.65		
	P1–H4		1.400		a	1087.10		
	P1–H5		1.400		a	1117.76		
	∠H4P1H5		100.0		a	1142.33		
	∠H4P1BH1		−179.1		a	1173.93		
	∠H5P1BH1		61.9		a	1176.94		
	P2–H6		1.410		a	2465.89		
	P2–H7		1.411		a	2480.90		
	∠H6P2P1		91.9		a	2486.22		
	∠H7P2P1		96.2		a	2521.58		
	∠H6P2P1B		−59.2		a	2533.06		
	∠H7P2P1B		−153.8		a	2569.71		
					a	2584.41		

[a] Bond lengths are given in angstroms and bond angles in degrees. [b] aV(T+d)Z fitting for PH and P$_2$. [c] Experimental values for PH, PH$_2$, PH$_3$, P$_2$, P$_2$H$_4$, and CH$_3$PH$_2$, taken from refs 34, 32 [estimated values], 28, 35, 36, and 37, respectively. [d] Harmonic frequency obtained from the fifth-order fitting of the PES at the CCSD(T)/aV(n+d)Z geometry, n = T and Q. [e] Anharmonic constant, $\omega_e\chi_e$, obtained from the fifth-order fitting of the PES at the CCSD(T)/aV(n+d)Z geometry, n = T and Q. [f] Optimization and frequencies for BH$_3$PH$_2$PH$_2$ calculated with MP2/aV(T+d)Z.

culation was initially performed and the spin constraint was relaxed in the coupled-cluster calculation.[40−42]

Core-valence corrections, ΔE_{CV}, were obtained at the CCSD-(T)/cc-pwCVTZ level.[43] Scalar relativistic corrections, ΔE_{SR}, which account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms, were evaluated at the CISD (configuration interaction singles and doubles) level of theory using the aV(T+d)Z basis set. ΔE_{SR} is taken as the sum of the mass−velocity and 1-electron Darwin (MVD) terms in the Breit−Pauli Hamiltonian.[44] For the phosphorus atom there is no atomic spin−orbit correction in its ^{4}S ground state, but a correction of 0.085 kcal/mol was taken for ΔE_{SO} of the carbon atom from the excitation energies of Moore.[45]

The total dissociation energy (ΣD_0 or TAE) of a compound is then given by the expression

$$\Sigma D_0 = \Delta E_{elec}(CBS) - \Delta E_{ZPE} + \Delta E_{CV} + \Delta E_{SR} + \Delta E_{SO} \quad (6)$$

using the components described above. We can calculate the molecular heats of formation at 0 K from the TAE and the known heats of formation at 0 K for the elements (ΔH_f^0(P) = 75.42 kcal/mol, ΔH_f^0(C) = 169.98 kcal/mol, ΔH_f^0(B) = 136.2 ± 0.2 kcal/mol, and ΔH_f^0(H) = 51.63 kcal/mol).[32] By following well established thermochemical procedures,[46] we can obtain gas phase heats of formation at 298 K.

Geometries for the substituted molecules with R = CH$_3$ were optimized at the B3LYP/aVTZ level. Harmonic vibrational frequencies for zero-point and thermal corrections were also obtained at this level. Second-order perturbation theory MP2

calculations[47] were subsequently performed using these geometries with the aV(n+d)Z basis sets n = D, T, and Q, and extrapolated to the CBS limit by using eq 4. We then used thefollowing isodesmic reactions to calculate the heats of formation of neutral methylated compounds.

$$CH_3PH_2 + P_2H_2 \rightarrow CH_3PPH + PH_3 \quad (7)$$

$$CH_3PH_2 + P_2H_4 \rightarrow CH_3HPPH_2 + PH_3 \quad (8)$$

$$2CH_3PH_2 + P_2H_2 \rightarrow CH_3PPCH_3 + 2PH_3 \quad (9)$$

$$2CH_3PH_2 + P_2H_4 \rightarrow$$
$$CH_3HPPHCH_3 \ (C_2 \ \text{symmetry}) + 2PH_3 \quad (10a)$$

$$2CH_3PH_2 + P_2H_4 \rightarrow$$
$$CH_3HPPHCH_3 \ (C_s \ \text{symmetry}) + 2PH_3 \quad (10b)$$

$$2CH_3PH_2 + P_2H_4 \rightarrow (CH_3)_2PPH_2 + 2PH_3 \quad (11)$$
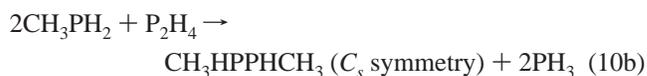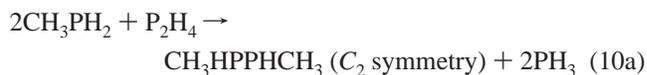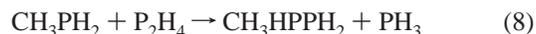
We also used isodesmic reactions to obtain the heats of formation of the following radicals.

$$CH_3PH_2 + H_2PP \rightarrow CH_3HPP + PH_3 \quad (12)$$

$$2CH_3PH_2 + H_2PP \rightarrow (CH_3)_2PP + 2PH_3 \quad (13)$$

The transition state structures for H$_2$ release from P$_2$H$_4$, without and with the assistance of a BH$_3$ molecule, were located at the B3LYP and MP2 levels for both systems and at the CCSD(T) level for P$_2$H$_4$, with the aVTZ basis set. Single-point
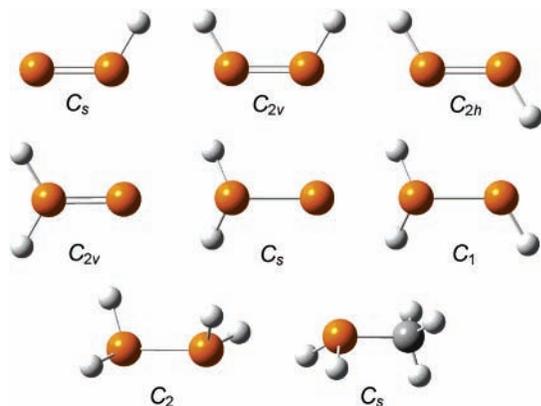
Figure 1. Optimized molecular structures and their symmetry point group for HP$_2$, *cis*-P$_2$H$_2$, *trans*-P$_2$H$_2$, H$_2$PP, ^{3}H$_2$PP, P$_2$H$_3$, P$_2$H$_4$, and CH$_3$PH$_2$.

CCSD(T) electronic energies were then computed to obtain the extrapolated CBS energies as outlined above.

For the kinetics of the H$_2$ elimination processes from P$_2$H$_4$, with and without BH$_3$ catalyst, we used transition state theory[48] (TST) and RRKM[49] as implemented in the KHIMERA program.[50] We used the MP2/aVTZ optimized geometry and scaled frequencies for the catalyzed reaction, and CCSD(T)/aVTZ geometry and MP2/aVTZ scaled frequencies for the noncatalyzed reaction. The CCSD(T)/CBS total electronic energies for the transition states and the reactants were used for both processes. We used the Skodje and Truhlar tunneling approximation,[51] which includes the imaginary frequency, the energy barrier, and the reaction energy, as given in eq 14 with $\Delta E^‡$ and ΔH_R the reaction exothermicity, both at 0 K

$$Q_{tunnel,ST}(T) = \frac{\beta\pi/\alpha}{\sin(\beta\pi/\alpha)} - \frac{\beta}{\alpha - \beta}\exp[(\beta - \alpha)(\Delta E^‡ - \Delta H_R)] \quad (14a)$$

This expression is valid for $\alpha \geq \beta$. In the case where $\beta \geq \alpha$

$$Q_{tunnel,ST}(T) = \frac{\beta}{\beta - \alpha}\{\exp[(\beta - \alpha)(\Delta E^‡ - \Delta H_R)] - 1\} \quad (14b)$$

with $\beta = 1/k_BT$ and $\alpha = 2\pi/h\omega_i$, ω_i is the imaginary frequency at the transition state. When the reaction is exoergic, ΔH_R is equal to zero.

Results and Discussion

Heats of Formation of P$_x$H$_y$ and CH$_3$PH$_2$ Compounds. Optimized CCSD(T) geometry parameters for the P$_x$H$_y$ and CH$_3$-PH$_2$ compounds with both aVTZ and aV(T+d)Z basis sets, as well as the MP2/aV(T+d)Z optimized geometry for the complex BH$_3$PH$_2$PH$_2$, are given in Table 1 and the diphosphorus hydrides and CH$_3$PH$_2$ molecules are shown in Figure 1. The CCSD(T) values obtained with both basis sets are similar to each other. For PH$_n$, with $n = 1-3$, their geometries obtained at the same levels were analyzed previously[4] and other calculations have been discussed in earlier papers.[31,52,53] The P$_2$H$_4$ molecule has a C_2 point group symmetry, in good agreement with experiment[8] and earlier calculations.[54,55] The P−P bond distance in P$_2$H$_4$ of 2.231 Å is about 0.2 Å longer than that in P$_2$H$_2$ (2.051 Å in the trans configuration and 2.061 Å in the cis), consistent with the nominal single bond character in the former and the nominal double bond character in the latter. The calculated P−P bond distance for P$_2$H$_4$ with the a(V+d)TZ basis set is still 0.013 Å

longer than the experimental value of 2.218 ± 0.004 Å from electron diffraction.[56] In contrast, the calculated P−H bond distance, 1.416 Å, is substantially shorter than that from the experiment, 1.451 ± 0.005 Å, suggesting a problem with the experimental value. The experimental HPP bond angle is 95.2 ± 0.6°, less than 1° larger than our calculated value of 94.5°, whereas the experimental HPH bond angle of 91.3 ± 1.4° is smaller than the calculated value of 94.0°.

As expected, the geometry of the radical P$_2$H is predicted to be bent with a ^{2}A′ ground state. The radical H$_2$PPH has only C_1 symmetry. The geometry of P$_2$H shows a P−H bond slightly stretched from that in *trans*-P$_2$H$_2$ and a P−P bond shortened from that in both *cis*- and *trans*-P$_2$H$_2$ by 0.02 Å but longer by 0.11 Å than that in P$_2$, which has formally triple bond character.

The calculated vibrational frequencies are also given in Table 1. Durig and co-workers[36] assigned all the observed vibrational fundamentals for the vibrational modes in P$_2$H$_4$. The agreement between the calculated and experimental values is reasonable with the calculated harmonic values higher than the experimental ones, which contain anharmonic contributions, as expected. For PH$_3$, P$_2$H$_4$, and CH$_3$PH$_2$ the scale resulting factors for the zero-point energies are 0.9849, 0.9837, and 0.9825, respectively, where the scale factor is defined as the ratio of the average of the CCSD(T) and experimental values divided by the CCSD-(T) value. The calculated P−P stretching frequency of 437.8 cm^{-1} for P$_2$H$_4$ compares well with the experimental fundamental[36] of 438 cm^{-1}. Yoshifuji and co-workers[57] recorded a P=P stretching frequency of 610 cm^{-1} from a resonance Raman study of a *trans*-(2,4,6-tri-*tert*-butylphenyl)diphosphene. The CCSD-(T) value of 599.2 cm^{-1} for this mode in *trans*-HP=PH is of comparable size, suggesting a small effect due to the substituents. The corresponding frequency in *cis*-HP=PH is slightly smaller, being 586.0 cm^{-1}. Singlet H$_2$P=P has a larger frequency (675.9 cm^{-1}) than that in HP=PH and triplet H$_2$P−P has a substantially smaller value (435.89 cm^{-1}). These results suggest a stronger PP bond in the planar singlet phosphinidene.

The energy components used in calculating the total dissociation energy to atoms (eq 6) are given in Table 2. Total energies are tabulated in Supporting Information The core-valence ΔE_{CV} corrections for the phosphorus hydrides are modest, ranging from 0.1 to 0.7 kcal/mol, and the scalar relativistic ΔE_{SR} corrections are of comparable magnitude but opposite in sign, ranging from −0.1 to −0.8 kcal/mol. The BH$_3$-PH$_2$PH$_2$ complex has the largest values with $\Delta E_{CV} = 2.03$ kcal/mol and $\Delta E_{SR} = -0.99$ kcal/mol.

The predicted heats of formation are given in Table 3, with estimated error bars of ±1.0 kcal/mol. The calculated heat of formation at 298 K for PH is in excellent agreement with that obtained by experiment[58] (56.8 vs 57.4 ± 0.6 kcal/mol). For PH$_2$, our calculated value differs by 1.3 kcal/mol with respect to the experimental value[58] (31.8 vs 33.1 ± 0.6 kcal/mol), somewhat larger than what might be expected. The calculated result for ΔH_f^0(PH$_3$, 298 K) is 1.1 kcal/mol and it is in excellent agreement with the experimental values[59] of 1.3 ± 0.4 and 1.1 ± 0.6 kcal/mol.[60,61] Our results at 298 K for PH, PH$_2$, and PH$_3$ are essentially the same as the earlier values obtained at the CCSD(T)/aVnZ ($n = 3-5$) level of theory by Ricca and Bauschlicher (ΔH_f^0(PH) = 56.8, ΔH_f^0(PH$_2$) = 31.8, and ΔH_f^0(PH$_3$) = 1.3, in kcal/mol),[53] and Haworth and Bacskay (ΔH_f^0(PH) = 56.6 ± 1.0, ΔH_f^0(PH$_2$) = 31.5 ± 1.0, and ΔH_f^0(PH$_3$) = 0.9 ± 1.0, in kcal/mol).[31] The heats of formation at 0 and 298 K for P$_2$ are in excellent agreement with the experimental values,[32] 35.1 vs 34.8 ± 0.5 kcal/mol and 34.7 vs 34.3 ± 0.5 kcal/mol, respectively. The calculated heat of

ΔH_f of Diphosphene, Phosphinophosphinidene, and Diphosphine

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TABLE 2: Calculated Total Atomization Energies at 0 K^a

molecule	CBS^b	ΔE_{ZPE}^c	ΔE_{CV}^d	ΔE_{SR}^e	ΣD_0^f
PH ($^3\Sigma^-$)	73.42^g	3.36^h	0.10	−0.11	70.04
PH$_2$ ($^2B_1$)	154.33	8.31^i	0.19	−0.23	145.98
PH$_3$ ($^1A_1$)	242.03	14.60	0.28	−0.36	227.34
P$_2$ ($^1\Sigma^+_g$)	116.33^g	1.12^h	0.65	−0.17	115.71
HP$_2$ ($^2A'$)	152.88	5.00^j	0.52	−0.34	148.06
trans-P$_2$H$_2$ (^1A_g)	234.24	10.85^j	0.55	−0.47	223.48
cis-P$_2$H$_2$ ($^1A_1$)	230.81	10.67^j	0.51	−0.48	220.16
H$_2$PP ($^1A_1$)	209.67	10.79^j	0.43	−0.78	198.54
H$_2$PP ($^3A''$)	206.47	10.67^j	0.45	−0.47	195.77
P$_2$H$_3$ (^2A)	286.53	15.54^j	0.52	−0.62	270.89
P$_2$H$_4$ (^1A)	370.25	21.76	0.55	−0.77	348.29
CH$_3$PH$_2$ ($^1A'$)	537.86	33.62^k	1.36	−0.62	504.92^l
BH$_3$PH$_2$PH$_2$	676.55	42.01^j	2.03	−0.99	635.55^m

^{a} Results are given in kcal/mol. ^{b} Extrapolated using eq 4 with aV(n+d)Z, where n = D, T, and Q. ^{c} The zero-point energies were obtained from the average of CCSD(T)/aVTZ and experimental values, when available, as reported in Table 1. See text for details. ^{d} Core/valence corrections were obtained with the cc-pwCVTZ basis sets at the CCSD(T)/aV(T+d)Z optimized geometries. ^{e} The scalar relativistic correction is based on a CISD/aV(T+d)Z calculation. ^{f} ΣD_0 computed with the CBS extrapolation obtained by using eq 6. ^{g} Extrapolated using eq 5 with aV(Q+d)Z and aV(5+d)Z. ^{h} ΔE_{ZPE} obtained from the fitting on the PES of the CCSD(T)/aV(Q+d)Z geometry. ^{i} A scale factor of 0.9849, obtained from PH$_3$, was used. ^{j} A scale factor of 0.9837, obtained from P$_2$H$_4$, was used. ^{k} The missing experimental frequency (see Table 1) was replaced by the calculated value. ^{l} Includes the spin−orbit correction for the C atom, −0.085 kcal/mol, obtained from ref 45. ^{m} Includes a spin−orbit correction of −0.03 for B.

TABLE 3: CCSD(T)/CBS Calculated and Experimental Heats of Formation at 0 and 298 K (kcal/mol)

molecule	ΔH_f (0 K)^a	ΔH_f^o(298 K)^a	ΔH_f^o(298 K) exptl
PH ($^3\Sigma^-$)	57.0	56.8	57.4 ± 0.6^d
			[60.6 ± 8.0]^b
PH$_2$ ($^2B_1$)	32.7	31.8	33.1 ± 0.6^d
			[30.1 ± 23.0]^b
PH$_3$ ($^1A_1$)	3.0	1.1	1.3 ± 0.4^f
			1.1 ± 0.6^g
P$_2$ ($^1\Sigma^+_g$)	35.2	34.7	34.3 ± 0.5^h
P$_2$H ($^2A'$)	54.4	53.4	
trans-P$_2$H$_2$ (^1A_g)	30.6	28.7	
cis-P$_2$H$_2$ ($^1A_1$)	33.9	32.0	
H$_2$PP ($^1A_1$)	55.6	53.7	
H$_2$PP ($^3A''$)	58.3	56.2	
P$_2$H$_3$ (^2A)	34.8	32.3	
P$_2$H$_4$ (^1A)	9.1	5.7	5.0 ± 1.0^i
CH$_3$PH$_2$ ($^1A'$)	−1.4	−5.0	
BH$_3$PH$_2$PH$_2$	12.9	7.5	
NH ($^3\Sigma^-$)	85.9^c	56.8	
NH$_2$ ($^2B_1$)	45.3^c	31.8	
NH$_3$ ($^1A_1$)	−9.1^e	1.1	−10.7^e
N$_2$ ($^1\Sigma^+_g$)	0.6^e	34.7	0.6^e
N$_2$H ($^2A'$)	60.8^e	53.4	60.1^e
trans-N$_2$H$_2$ (^1A_g)	49.9^e	28.7	48.1^e
cis-N$_2$H$_2$ ($^1A_1$)	54.9^e	32.0	53.2^e
H$_2$NN ($^1A_1$)		53.7	
H$_2$NN ($^3A''$)		56.2	
N$_2$H$_3$ (^2A)	56.2^e	32.3	53.7^e
N$_2$H$_4$ (^1A)	26.6^e	5.7	23.1^e
CH$_3$NH$_2$ ($^1A'$)	−1.4^j	−5.0	−4.7^j

^{a} Estimated error bar of ±1.0 kcal/mol. ^{b} Estimated values from ref 32. At 0 K, ΔH_f(PH) = [60.8 ± 8.0] and ΔH_f(PH$_2$) = [30.7 ± 23.0] kcal/mol. ^{c} Reference 63. ^{d} Reference 58. ^{e} Reference 6. ^{f} Reference 59. ^{g} References 60 and 61. ^{h} Reference 32. At 0 K, ΔH_f(P$_2$) = 34.8 ± 0.5 kcal/mol. ^{i} References 59 and 62. ^{j} Reference 64.

formation of 5.7 kcal/mol for P$_2$H$_4$ at 298 K is in excellent agreement with the experimental value[62] of 5.0 ± 1.0 kcal/mol. Our results at 298 K for P$_2$, trans-P$_2$H$_2$, and P$_2$H$_4$ are higher than the theoretical values obtained by Haworth and Bacskay,

but within their suggested error bars (ΔH_f^o(P$_2$) = 34.4 ± 1.0, ΔH_f^o(P$_2$H$_2$) = 28.1 ± 1.0, and ΔH_f^o(P$_2$H$_4$) = 4.9 ± 2.0 kcal/mol).[31] Our calculated value for ΔH_f^o(CH$_3$PH$_2$) is −5.0 and, to our knowledge, no experimental data are available. cis-P$_2$H$_2$ is predicted to be less stable than the trans by 3.3 kcal/mol. The heats of formation of ΔH_f^o(P$_2$H) = 53.4, ΔH_f^o(H$_2$PP) = 53.7, ΔH_f^o(^{3}H$_2$PP) = 64.2, and ΔH_f^o(P$_2$H$_3$) = 32.3 have not been reported previously. For further discussion, previously calculated heats of formation of the analogous nitrogen molecules[6,63,64] are also shown in Table 3.

For the P$_2$H$_2$ isomers, trans-diphosphene is 25.0 kcal/mol more stable than phosphinophosphinidene. We predict the ground electronic state of H$_2$PP to be a singlet with a singlet−triplet energy gap of 2.8 kcal/mol ($^1A_1 \rightarrow {}^3A''$). Previous lower level calculations predicted a triplet ground state for H$_2$PP. Allen et al.[14] obtained a singlet−triplet difference of 7.2 kcal/mol with CISD wavefunctions and HF/DZ and HF/DZ+P geometries. Similar differences were calculated by Nguyen,[12a] at the MP4SDQ/6-31++G*//HF/3-21G* level (6.7 kcal/mol), and by Ito and Nagase,[65] employing MP3/6-31G**//HF/6-31G* and HF/3-21G ZPE calculations (6.2 kcal/mol). A smaller difference, 3.0 kcal/mol, was predicted by Schmidt and Gordon[13] at the SOCI/6-31G* level. More recently, Nguyen et al.[12b] predicted the singlet state to be higher than the triplet by only 1.2 kcal/mol at the QCISD(T)/6-311++G(3df,2p) level. The singlet−triplet splitting is quite sensitive to the level of calculation, especially the quality of the basis set. At the CCSD(T)/aVDZ level, the triplet is lower than the singlet, but with the larger aVTZ basis set, the singlet is below the triplet. This ordering is maintained with the aVQZ basis set and at the extrapolated CBS limit. The singlet−triplet gap in PH is 28 kcal/mol favoring the triplet,[12b] so substitution of the hydrogen by the phosphino group H$_2$P stabilized the singlet by at least 30 kcal/mol as compared to the triplet by electron delocalization from its P lone pair into the empty P(π) orbitals of the monocoordinated P atom.

We can compare our P−H bond dissociation energies (BDE in kcal/mol), at 0 K, to the experimental[66] values: BDE(H−PH$_2$) = 81.3 vs 82.46 ± 0.46, BDE(H−PH) = 75.9 vs 74.2 ± 2.0, and BDE(H−P) = 70.1 vs 70.5 ± 2.0. We found that the BDEs are all in very good agreement with experiment, with the largest difference for PH$_3$ due to the difference in (ΔH_f-(PH$_2$).[66] Our values are very similar to those previously calculated by a comparable method:[67] BDE(H−PH$_2$) = 81.0 and BDE(H−PH) = 75.9 kcal/mol. Our BDE values in P$_2$H, P$_2$H$_2$, P$_2$H$_3$, and P$_2$H$_4$ are 32.3, 75.4, 47.4, and 77.3 kcal/mol, respectively. The P−H bond strengths in the P$_2$H and P$_2$H$_3$ radicals are ∼30 kcal/mol lower than those in P$_2$H$_2$ and P$_2$H$_4$, respectively. The BDE of PH$_2$ is larger than the BDE's in P$_2$H and P$_2$H$_3$ by 43.6 and 28.5 kcal/mol, respectively. In contrast, the BDE in PH$_2$ differs from those in P$_2$H$_2$ and P$_2$H$_4$ by only +0.5 and −1.4 kcal/mol, respectively.

If we compare the P−H BDEs with respect to the N−H BDEs from the corresponding nitrogen compounds,[6] we find that the NH$_n$ ($n = 1-3$) species show the same trend as the PH$_n$; i.e., the higher the number of hydrogen atoms in the molecule, the stronger the bond (kcal/mol): BDE(H−NH$_2$) = 106.0; BDE-(H−NH) = 92.3; BDE(H−N) = 78.2. For P$_2$H$_2$, the P−H BDE-(H−PPH) is stronger than N−H BDE in N$_2$H$_2$ by 12.9 kcal/mol. The P−H BDE in P$_2$H$_4$ is weaker than the N−H BDE in N$_2$H$_4$ by 3.9 kcal/mol. These differences are probably due to changes in the P−P and N−N bond energies as discussed below.

The trends in P−P bond strengths can be compared to our previous studies of N−N results.[6] The P−P bond strength in

P_2 is 115.7 kcal/mol (nominal triple bond), in *trans*-HPPH is 83.4 kcal/mol (nominal double bond) and in H_2PPH_2 is 56.3 kcal/mol (nominal single bond). This last result is 3.4 kcal/mol lower than the estimated experimental value[66] of 59.7 ± 1.2 kcal/mol. The corresponding N−N bond strengths are 225.1 kcal/mol in N_2, 121.9 kcal/mol in HNNH, and 63.9 kcal/mol in H_2NNH_2. Thus the NN triple and double bonds are much stronger than the PP triple and double bonds but the NN and PP single bonds are of comparable energy. This is due to weaker overlap between the $3p(\pi)$ orbitals of phosphorus atoms in forming multiple P−P bonds as compared to the overlap of the 2p orbitals in the nitrogen compounds. This is consistent with the result that diphosphines form a class of stable compounds whereas diphosphenes are only isolable with substantial steric protecting groups.

Molecular entropies are given in Table S1 of the Supporting Information. The calculated energies for some simple hydrogenation reactions are (using a calculated value of $\Delta H_f(H_2) = -0.1$ kcal/mol at 298 K).

$$P_2 + H_2 \rightarrow P_2H_2$$
$$\Delta H(298 \text{ K}) = -6.1 \text{ kcal/mol}; \Delta G(298 \text{ K}) = 1.0 \text{ kcal/mol} \quad (15)$$

$$P_2H_2 + H_2 \rightarrow P_2H_4$$
$$\Delta H(298 \text{ K}) = -23.1 \text{ kcal/mol}; \Delta G(298 \text{ K}) = -15.5 \text{ kcal/mol} \quad (16)$$
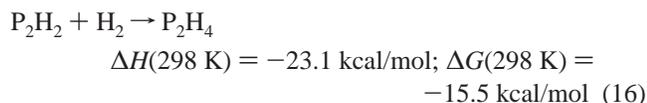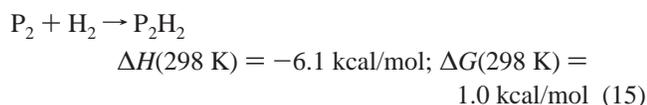
From our previous work,[6] we obtained

$$N_2 + H_2 \rightarrow N_2H_2$$
$$\Delta H(298 \text{ K}) = 47.6 \text{ kcal/mol}; \Delta G(298 \text{ K}) = 55.0 \text{ kcal/mol} \quad (17)$$

$$N_2H_2 + H_2 \rightarrow N_2H_4 \quad \Delta H(298 \text{ K}) = -24.9 \text{ kcal/mol}; \Delta G(298 \text{ K}) = -16.5 \text{ kcal/mol} \quad (18)$$
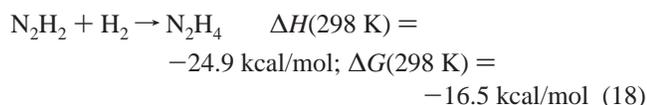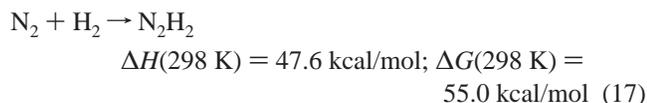
The hydrogenation of N_2 is an endothermic reaction and differs by more than 50 kcal/mol from the analogous phosphorus analogue, which is slightly exothermic. This is due to the large differences in the NN and PP triple bond energies. Reactions 16 and 18 have essentially the same energetics. Hydrogenation of P_2H_4 and P_2H_2 to form two PH_3 molecules (reactions 19 and 20, respectively) are exothermic processes.

$$P_2H_4 + H_2 \rightarrow 2PH_3$$
$$\Delta H(298 \text{ K}) = -3.6 \text{ kcal/mol}; \Delta G(298 \text{ K}) = -4.8 \text{ kcal/mol} \quad (19)$$

$$P_2H_2 + 2H_2 \rightarrow 2PH_3$$
$$\Delta H(298 \text{ K}) = -26.7 \text{ kcal/mol}; \Delta G(298 \text{ K}) = -20.3 \text{ kcal/mol} \quad (20)$$
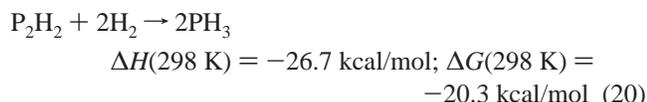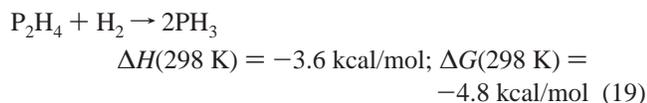
We previously calculated the analogous reactions with nitrogen compounds[6] and obtained

$$N_2H_4 + H_2 \rightarrow 2NH_3$$
$$\Delta H(298 \text{ K}) = -44.4, \Delta G(298 \text{ K}) = -47.9 \text{ kcal/mol} \quad (21)$$

$$N_2H_2 + 2H_2 \rightarrow 2NH_3$$
$$\Delta H(298 \text{ K}) = -69.3 \text{ kcal/mol}; \Delta G(298 \text{ K}) = -64.4 \text{ kcal/mol} \quad (22)$$
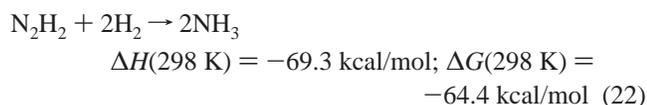
TABLE 4: Calculated Reaction Enthalpies (kcal/mol) at 298 K for Reactions 7−13[a]

reaction	B3LYP/aVTZ	MP2/CBS[b]
7	−2.44	−3.17
8	−0.76	−1.47
9	−3.97	−5.58
10a	−1.45	−3.74
10b	0.58	−1.20
11	−3.31	−6.23
12	−6.50	−7.82
13	−12.08	−15.32

[a] The thermal corrections to the enthalpies at the MP2 level for calculating $\Delta H(298 \text{ K})$ were taken from B3LYP/aVTZ calculations. *[b]* MP2/CBS(1) + ZPE (B3LYP/aVTZ) = $\Delta H°(0 \text{ K})$: −3.56 (reaction 7), −1.86 (reaction 8), −6.52 (reaction 9), −4.44 (reaction 10a), −1.97 (reaction 10b), −6.97 (reaction 11), −8.13 (reaction 12), −16.08 (reaction 13) kcal/mol.

Reactions 21 and 22 are substantially more exothermic than reactions 19 and 20, respectively. We can predict the hydrogenation reaction for methylphosphine (CH_3PH_2) to form PH_3 and CH_4 using the experimental heat of formation and entropy for CH_4[68] of $\Delta H_f(CH_4, 298 \text{ K}) = -17.80$ kcal/mol and $S(CH_4) = 44.55$ cal/(mol·K).

$$CH_3PH_2 + H_2 \rightarrow PH_3 + CH_4$$
$$\Delta H(298 \text{ K}) = -11.8 \text{ kcal/mol}; \Delta G(298 \text{ K}) = -12.4 \text{ kcal/mol} \quad (23)$$
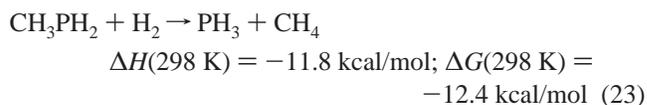
The predicted heat of reaction is about 6 kcal/mol more exothermic than a previous MP2 value of −5.6 kcal/mol.[30]

Heats of Formation of Methyl Derivatives. To estimate the heats of formation for *trans*-CH_3PPH, CH_3HPPH_2, *trans*-CH_3-$PPCH_3$, $CH_3HPPHCH_3$ (C_2 and C_s) $(CH_3)_2PPH_2$, CH_3HPP, and $(CH_3)_2PP$, we calculated the MP2/CBS energy of the isodesmic reactions 7−13 and used our computed values for PH_3, P_2H_2, P_2H_4, and CH_3PH_2 (the MP2 electronic energies are in Table S2 of the Supporting Information). For methylphosphinidenes, we considered only the singlet state, because in methyl derivatives, the singlet state has been found to be the ground state.[12b] The results for the reaction energies at the B3LYP/aVTZ and MP2/CBS levels are given in Table 4 (More detailed information can be found in Table S3 of the Supporting Information.) The MP2 reaction energies have a small basis set dependence ranging from 0.2 to 1.0 kcal/mol. Larger differences are found between the B3LYP and MP2/CBS results of up to 4 kcal/mol.

We can compare the reaction energies of (7), (9), and (10a) with the three following reactions at 298 K (kcal/mol)

$$CH_3NH_2 + N_2H_2 \rightarrow CH_3NNH + NH_3$$
$$\Delta H = -12.2 \text{ kcal/mol} \quad (24)$$

$$2CH_3NH_2 + N_2H_2 \rightarrow CH_3NNCH_3 + 2NH_3$$
$$\Delta H = -24.0 \text{ kcal/mol} \quad (25)$$

$$2CH_3NH_2 + N_2H_4 \rightarrow CH_3HNNHCH_3 \text{ (C_2 symmetry) } + 2NH_3 \quad \Delta H = -12.7 \text{ kcal/mol} \quad (26)$$

The nitrogen reactions are more exothermic than the phosphorus ones by 9.0, 18.4, and 9.0 kcal/mol, respectively.

The estimated heats of formation for the methylated species are shown in Table 5, with an estimated error bar of ±2.0 kcal/mol. Our heats of formation for the methyl derivatives allow us to predict the hydrogenation energy of the following reaction

ΔH_f of Diphosphene, Phosphinophosphinidene, and Diphosphine

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TABLE 5: Heats of Formation from Isodesmic Reactions at 0 and 298 K (kcal/mol)[a]

molecule	reaction	$\Delta H_f(0 \text{ K})$	$\Delta H_f^{\circ}(298 \text{ K})$
trans-CH$_3$PPH	7	22.6	19.4
CH$_3$HPPH$_2$	8	2.8	−1.9
trans-CH$_3$PPCH$_3$	9	15.3	10.9
CH$_3$HPPHCH$_3$ (C_2)	10a	−4.1	−10.2
CH$_3$HPPHCH$_3$ (C_s)	10b	−1.7	−7.7
(CH$_3$)$_2$PPH$_2$	11	−6.7	−12.7
CH$_3$HPP	12	43.1	39.8
(CH$_3$)$_2$PP	13	30.7	26.2

[a] MP2/CBS electronic energies with ZPE and thermal corrections to the enthalpies at the B3LYP/aVTZ.
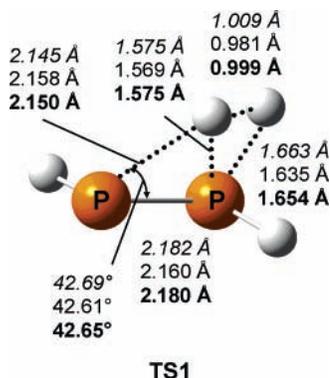
Figure 2. Optimized transition structure **TS1** for H$_2$-elimination from P$_2$H$_4$. Bond lengths are given in Å and bond angles in degrees. Upper values: B3LYP. Middle: MP2. Lower: CCSD(T). All with the aug-cc-pVTZ basis set.

at 298 K

$$CH_3PPCH_3 + H_2 \rightarrow CH_3HPPHCH_3$$
$$\Delta H = -19.8 \text{ kcal/mol}; \Delta G = -11.1 \text{ kcal/mol} \quad (27)$$
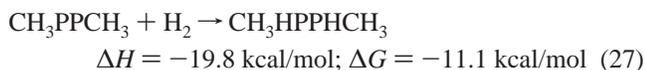
The entropy values were obtained at the B3LYP/aVTZ level (Table S4 of the Supporting Information). Comparison with reaction 16 shows that the introduction of methyl groups moves the reaction closer to thermoneutral but not by as much as in the nitrogen analog. Reaction 27 is more exothermic by 6.0 kcal/mol in comparison to the nitrogen reaction.[6]

Mechanism for H$_2$ Release from Diphosphine. For a compound to be useful as a hydrogen system, besides thermodynamic considerations, it is also necessary to have good kinetics for the release of H$_2$. To determine the activation parameters associated with the molecular hydrogen release in a parent compound, we have located the transition structure (TS) for a [2+2] loss of H$_2$ from diphosphine (P$_2$H$_4$). In a recent study,[7] we showed that generation of H$_2$ from ethane and ammonia borane is greatly accelerated by the assistance of a borane molecule (BH$_3$). The Lewis acid BH$_3$ exerts a substantial catalytic effect, via a bifunctional process of giving and receiving H atoms, which facilitates H transfer and H$_2$ formation. To probe further this catalytic behavior, we also found the TS for H$_2$ release from P$_2$H$_4$ catalyzed by BH$_3$.

Geometry parameters of the **TS1** for H$_2$ release from P$_2$H$_4$ were optimized at the B3LYP, MP2, and CCSD(T) levels with the aVTZ basis set. Important geometry parameters are displayed in Figure 2. For the transition state, **TS−BH$_3$**, for the P$_2$H$_4$ + BH$_3$ reaction, we only optimized the geometry at the B3LYP and MP2 levels as shown in Figure 3. The stationary points were characterized by harmonic vibrational frequencies computed at the MP2 level. The MP2/aVTZ geometries were then used to obtain the CCSD(T)/CBS energies (Table S5 of the
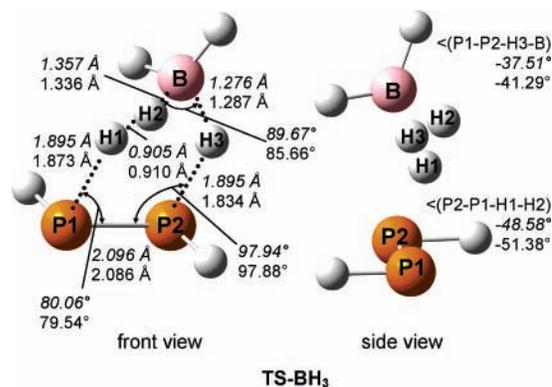

Figure 3. Optimized transition structure **TS−BH$_3$** for H$_2$-elimination from P$_2$H$_4$ with the assistance of BH$_3$. Bond lengths are given in Å and bond angles in degrees. Upper values: B3LYP. Lower: MP2. Both with the aug-cc-pVTZ basis set.

TABLE 6: Calculated Energy Barrier ($\Delta E^{\ddagger}$, kcal/mol) for the H$_2$-Release Processes in P$_2$H$_4$, without and with the BH$_3$, at Different Levels of Theory

theory[a]	$\Delta E^{\ddagger}$ (P$_2$H$_4$)	$\Delta E^{\ddagger}$ (P$_2$H$_4$ + BH$_3$)[b]
CCSD(T)/aVDZ	74.3	38.9
CCSD(T)/aVTZ	72.6	38.1
CCSD(T)/aVQZ	72.5	38.3
CCSD(T)/CBS	72.5	38.5

[a] Including zero-point energies obtained from MP2/aVTZ and scaled by a factor of 0.9837. Uncorrected ZPE values (kcal/mol): P$_2$H$_4$, 22.6; P$_2$H$_4$(TS), 19.8; BH$_3$, 16.8; P$_2$H$_4$−BH$_3$ (TS), 39.5. [b] Energy barrier with respect to the separated P$_2$H$_4$ + BH$_3$ reactants. To obtain the energy barrier with respect to the complex, add 22.6 kcal/mol.

Supporting Information). The barrier heights for both processes obtained at different levels are summarized in Table 6. The CCSD(T) barrier heights are well converged with respect to the basis set, and the values computed using the aVTZ basis set, computationally much less demanding than those using the aVQZ set, are quite close to the corresponding CBS values, differing by 0.1 kcal/mol in P$_2$H$_4$ and by 0.4 kcal/mol in the P$_2$H$_4$ + BH$_3$ system. A higher barrier of 87.1 kcal/mol was predicted[13] for this process at the MP4SDQ/6-31G(d,p)//HF/3-21G(d) level.

The geometries of **TS1** derived from the three different methods are comparable to each other with variations in bond distances of up to 0.02 Å and in bond angles of up to 3°. The four P−P−H−H atoms in **TS1** are found to lie in the same molecular plane. Although this formally corresponds to a TS for a [2+2] elimination yielding H$_2$ plus HP=PH, the two departing H atoms are essentially connected to one P atom. This is similar to the situation in the TS's for H$_2$ loss in ethane and ammonia borane.[7] Within the three-membered P−H−H cycle of **TS1**, the H−H distance of the departing H$_2$ is 1.0 Å, and the two P−H distances are 1.58 and 1.65 Å. Compared with the distances of 0.75 Å of free H$_2$ and 1.41 Å of a normal P−H bond, the values suggest significant P−H bond breaking in **TS1**, which results in a substantial energy barrier of 72.5 kcal/mol. The energy of the **TS1** can be estimated by considering a rearrangement process involving the breaking of two P−H bonds and forming an H−H bond leading to an estimate of 51.4 kcal/mol (taking the calculated values BDE(P−H) = 77.3 kcal/mol in P$_2$H$_4$ and BDE(H−H) = 103.2 kcal/mol in H$_2$). The actual calculated barrier is 21.1 kcal/mol larger than this simple estimate.

Initially, P$_2$H$_4$ and BH$_3$ will form a strong complex, as shown in Figure 4 due to the formation of a dative σ bond between the lone pair acceptor BH$_3$ and the electron pair donor PH$_2$-
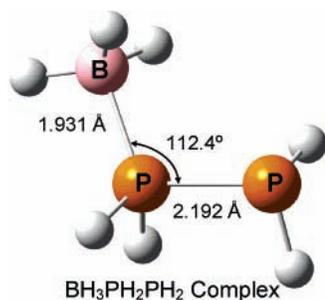
Figure 4. Optimized molecular structure for the complex BH_3PH_2-PH_2 at the MP2/aug-cc-p(V+d)TZ level.

PH_2. The binding energy of the complex is 23.7 kcal/mol at 298 K, slightly higher than the value of 21.1 kcal/mol for BH_3-PH_3.[4] Thus substitution of the H by PH_2 in PH_3 raises the binding energy by 2.6 kcal/mol. However, the complex is not oriented so as to enable H_2 elimination from PH_2PH_2 but may be oriented so that elimination of H_2 could occur across the P−B bond. We did not study this latter process.

We studied the reaction pathway starting from the separated P_2H_4 + BH_3 system and passing through **TS−BH₃**. The shape of **TS−BH₃** is similar to the transition state structures obtained in our previous study[7] for the C_2H_6 + BH_3 and BH_3NH_3 + BH_3 reactions. **TS−BH₃** involves a cyclic structure with B−H−H−P and B−H−P arrangements dominating the two main motions of the nuclei. The H2 atom of BH_3 approaches the H1 atom of P_2H_4 to form the departing H_2 molecule. The H3 atom of diphosphine is transferred in a concerted manner from P2 to B, regenerating BH_3. The energy barrier via **TS−BH₃** is calculated to be 38.5 kcal/mol at the CCSD(T)/CBS level, with respect to the separated P_2H_4 + BH_3 reactants (Table 6). The ZPE values were scaled by a factor of 0.9837 from P_2H_4. Relative to the H_2 elimination from P_2H_4 via **TS1**, the BH_3 catalyzed process leads to a substantial decrease of 34.0 kcal/mol in the barrier height. Overall, these results tend to confirm our recent result that the Lewis acid BH_3 can serve as a bifunctional catalyst for the H_2 elimination. However, due to the possibility of complex formation, an overpressure of BH_3 might be needed for the catalyzed process to occur. Even though the thermodynamics are not favorable for release of H_2 from P_2H_4, the energy barrier in the presence of the Lewis acid catalyst BH_3 is substantially reduced. Including the 15.5 kcal/mol endothermicity of the reaction, the additional barrier is only 23.0 kcal/mol. As noted above, with appropriate substituents, the endothermicity can be substantially reduced. Presumably, the barrier will also be reduced so that the H_2 can be generated under milder thermal conditions. In addition, medium effects play an important role. Studies of such processes will be undertaken in our laboratory.

We analyzed the kinetics for H_2 elimination from P_2H_4 without BH_3 as the reaction catalyst using our calculated stationary points on the potential energy surface. We calculated the rates over a temperature (*T*) range of 200−2000 K and the pressure of the bath gas (*p*) from 0.1 to 8360 Torr by using RRKM theory (Supporting Information). For this range of *T* and *p* with N_2 as the collision gas, the calculated data can be fit to the general expression

$$k(T,p) = 2.0 \times 10^{12} p^{0.221} \exp \frac{-74.8}{RT} \qquad (28)$$

At 298 K and 760 Torr (1 atm), $k = 9.4 \times 10^{-43}$ s^{-1}; the same result was found at 11 atm, so that the high-pressure limit was

reached at 1 atm. A similar result is obtained with TST at 298 K, $k_\infty = 8.4 \times 10^{-43}$ s^{-1}, as expected.

For the bimolecular BH_3 catalyzed reaction, we obtained $k_{\infty,\text{catalyzed}} = 4.6 \times 10^{-20}$ cm^3·mol^{-1}·s^{-1} applying TST starting from the dissociated reactants. The rate constant for the catalyzed reaction is 5.5×10^{22} times faster than the noncatalyzed result starting from the separated reactants. We used RRKM theory to analyze the kinetics starting from the complex $BH_3PH_2PH_2$. Using the above pressure and temperature ranges, we obtained

$$k(T,p) = 3.2 \times 10^{12} p^{0.136} \exp \frac{-62.9}{RT} \qquad (29)$$

The rate constant at the high-pressure limit is 5.4×10^{-34} s^{-1} at 298 K from TST and is 6.0×10^{-34} s^{-1} from RRKM theory. Even if the BH_3 forms an initial complex with the PH_2PH_2 which is quenched by collisions, the catalyzed reaction is still 9 orders of magnitude faster than the uncatalyzed one.

The uncatalyzed transition state is characterized by an imaginary frequency of 1593i cm^{-1} and the catalyzed transition state by one of 1053i cm^{-1}. The tunneling factors for both H_2 elimination processes are given in Table S6 of the Supporting Information). For the noncatalyzed reaction, $Q_{\text{tunnel}} = 5.45 \times 10^7$ at 298 K, which gives us a corrected RRKM rate constant of $k = 5.1 \times 10^{-35}$ s^{-1}, and a corrected TST rate constant, $k_\infty = 4.6 \times 10^{-35}$ s^{-1}. For the catalyzed reaction at 298 K starting from separated reactants, $Q_{\text{tunnel,catalyzed}} = 4.5$, giving $k_{\infty,\text{catalyzed}} = 2.1 \times 10^{-19}$ cm^3·mol^{-1}·s^{-1}. In this case, the corrected rate constant for the catalyzed reaction is 4.5×10^{15} times faster. The tunneling factor for the uncatalyzed reaction is very large; however, this approximation is very reliable and large tunneling corrections have been previously found.[69]

Conclusion

The heats of formation of P_2H_x compounds were calculated by using ab initio molecular orbital theory at the CCSD(T)/CBS level. Our calculated results are in excellent agreement with the available experimental values. We calculated the heats of formation of $P_2(H)_x(CH_3)_y$ molecules by using an isodesmic reaction approach with reaction energies calculated at the MP2/CBS level. We found a singlet ground state for the H_2PP radical with a singlet−triplet energy gap of 2.8 kcal/mol, showing that phosphinophosphinidene is similar to aminonitrene, H_2NN, which has a singlet ground state. The corrected rate constant (including tunneling) for the catalyzed reaction is predicted to be 4.5×10^{15} times faster than the noncatalyzed result. The calculated results for the hydrogenation reactions show that substitution of an alkyl or aryl substituent for H improves the reaction energies, suggesting that substituted phosphorus compounds could possibly be used in a chemical hydrogen storage system although there is an associated weight penalty.

Supporting Information Available: CCSD(T) energies (E_h), zero-point energies (ZPE in kcal/mol), thermal corrections (TC in kcal/mol) and entropies (S in cal/(mol·K)) for PH_n, P_2H_m, CH_3PH_2, and $BH_3PH_2PH_2$. B3LYP/aVTZ (E_h) and MP2 (E_h)

as a function of basis set extrapolated to the complete basis set limit. Comparison of energies and enthalpies (kcal/mol) for reactions 7−13. B3LYP/aVTZ ZPE, TC, heats of formation, and *S* of methylated compounds. CCSD(T) energies (E_h) and tunneling corrections for the H_2-release processes. 3-D plots of the rate coefficients *k* of the for the H_2 elimination from P_2H_4 and for the B−P bond dissociation of the $BH_3PH_2PH_2$ complex calculated by using RRKM theory with N_2 as the bath gas. This material is available free of charge via the Internet at http://pubs.acs.org.

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