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A G2 Study on CH Insertions into PH_3, H_2S, and HCl

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The insertions of methylidyne into PH_3, H_2S, HCl, NH_3, H_2O, and HF have been systematically studied at the MP4/6-311++G(2d,p)//MP2/6-311++G(d,p) + ZPEs and G2 levels. Each of the insertions is predicted to occur via an initially formed intermediate complex $HC{-}XH_n$ followed by a hydrogen-migration process. By comparison of the energetic and geometrical results of these insertions, two three-point sets of rules (rules A and rules B) are found and discussed, which are compared with those for the SiH insertions. Interestingly, the complexes $HC{-}PH_3$ and $HC{-}SH_2$ are found not to be the simple (loosely bound) donor−acceptor complexes as those formed in the CH insertions into other hydrides and those formed in the SiH insertions are. Their molecular and electronic structures have the following features: the short C−X bond lengths (1.723 and 1.751 Å, being shorter than or comparable to the bond lengths 1.787 and 1.724 Å in the corresponding products); large binding energies (47.5 and 25.8 kcal/mol, respectively); considerable charge separations; and low rotational barriers around C−X bonds. On the basis of the detailed comparison with the qualitative features of typical ylides ($H_2C{-}PH_3$ and $H_2C{-}SH_2$), $HC{-}PH_3$ and $HC{-}SH_2$ are considered to be similar to the ylides in nature, being "ylide-like radicals". We suggest the two radicals might be observed in some experiments since they are in deep wells in the energy surface. The calculated dipole moments and hyperfine coupling constants are reported.

Introduction

Methylidyne (CH), known to be one of the most reactive of all radicals,[1] is important in combustion and planetary atmospheric chemistry. The fundamental significance of this radical has stimulated numerous kinetic studies on its reactions.[1] Ab initio theoretical studies could give detailed descriptions of reaction mechanisms. As an important class of reactions in the chemistry of methylidyne, the insertions of CH into compounds were the subjects of several theoretical papers[2−7] that show unexpected situations and complexities in the reaction paths.

In our previous paper, the insertions of CH into NH_3, H_2O, and HF were investigated at the MP2(FU)/6-31G(d,p) + ZPEs level.[6] The energetic results indicate that the insertion channels are energetically favorable, which are in agreement with the conclusions based on kinetic experiments.[1,8] The predicted mechanisms for the insertions of CH into NH_3, H_2O, and HF can be illustrated by eqs 4−6 given below

$$\underset{(\mathbf{ma})}{CH + XH_n} \rightarrow \underset{(\mathbf{mb})}{HC{-}XH_n} \rightarrow \underset{(\mathbf{mc})}{TS} \rightarrow \underset{(\mathbf{md})}{H_2CXH_{n-1}}$$

(1) $X = P$, $n = 3$; (2) $X = S$, $n = 2$; (3) $X = Cl$, $n = 1$;
(4) $X = N$, $n = 3$; (5) $X = O$, $n = 2$; (6) $X = F$, $n = 1$

where the reactants, intermediate complexes ($HC{-}XH_n$), transition states (TS), and insertion products (H_2CXH_{n-1}) are denoted as **ma**, **mb**, **mc**, and **md** (m = 4, 5, and 6), respectively.

Recently we performed ab initio calculations for the insertions of CH into PH_3, H_2S, and HCl. The skeletons of the energy profiles representing the reaction paths for the CH insertions into these second-row hydrides are similar to those for the insertions into the respective first-row hydrides,[6] being illustrated by eq 1−(3) (given above), respectively. However, the intermediate complexes $HC{-}PH_3$ (**1b**) and $HC{-}SH_2$ (**2b**) initially formed in reactions 1 and 2 are not the simple complexes, being similar to the phosphonium and sulfonium ylides (the P- and S-ylides) in nature. We call the two complexes "ylide-like complexes", which were simply reported in *Chem. Commun.*[9] In the present study we perform a systematic study on the CH insertions into PH_3, H_2O, HCl, NH_3, H_2O, and HF at the G2 level. First, we draw some rules for these CH insertions and compare them with those for the SiH insertions, and then we discuss and describe molecular and electronic structures of **1b** and **2b** in comparison with the P- and S-ylides.

Computational Details

The Gaussian 94 program[10] was used to perfom ab initio molecular calculations. The G2 calculations in the present study are slightly different from the standard G2[11] calculations. Because we failed in locating transition states for some reactions at the HF/6-31G(d) level, the MP2(FU)/6-31G(d) frequency calculations were employed to characterize the stationary points under investigations and estimate the contributions of zero point energies (ZPEs, scaled by a factor of 0.9646[12]) to the relative energies at the various levels used in this paper. To get more reliable geometries, all structures were reoptimized at the MP2(FC)/6-311++G(d,p) level. The single point calculations MP4(FC)/6-311++G(2d,p)//MP2/6-311++G(d,p) were performed for the purpose of comparison with the SiH insertions.[13] It is noted that, in our previous paper,[13] the single point energies are corrected with the HF/6-31G(d) ZPEs, which is assumed not to influence our conclusions.

For the open-shell systems under consideration, the expectation values of the S^2 operator were checked in the (U)MP2(FC)/6-311++G(d,p) calculations and the $\langle S^2 \rangle$ values were all

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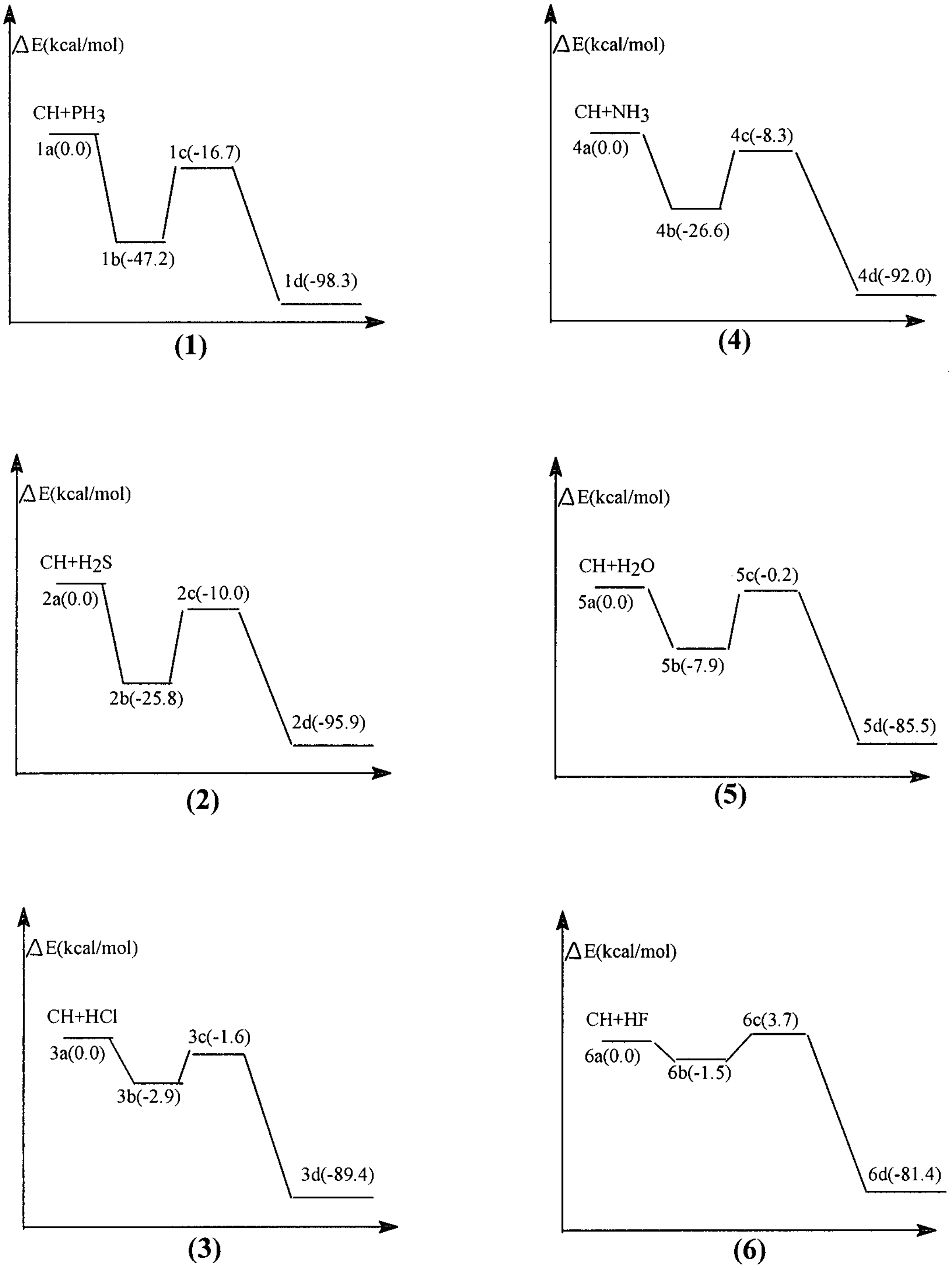

Figure 1. Schematic diagram of the potential energy curves of the CH insertion reactions with PH_3 (1), H_2S (2), HCl (3), NH_3 (4), H_2O (5), and HF (6). The values in parentheses are the G2 relative energies in kcal/mol (corrected with the MP2/6-31G(d) zero-point energies).

smaller than 0.8 except for the value (0.87) for **6b**. As we did in the previous study, the spin-projected energetic results are used.

Results and Discussion

The potential energy curves shown in parts (1)−(6) of Figure 1 represent schematically the calculated insertion paths for reactions 1−6, respectively, and the G2 energies of **mb**, **mc**, and **md** relative to **ma** ($m = 1-6$, respectively) are given. The energy profiles indicate each of the insertions takes place via an initially formed intermediate complex followed by a hydrogen migration process. The structures of **mb**, **mc**, and **md** ($m = 1-6$), optimized at the two levels, are displayed in Figure 2. In Table 1 are listed the relative energies calculated at the three levels, together with the MP2(FU)/6-31G(d) ZPEs, the MP2-(FU)/6-31G(d)) imaginary frequencies for the transition states, and the MP2(FC)/6-311++G(d,p) $\langle S^2 \rangle$ expectation values. The term “relative energy” (of a species) in the following means “the energy of a species relative to the reactant in the same reaction”. In the following discussion, the G2 energies and the MP2(FC)/6-311++G(d,p) geometries are used unless otherwise noted.

1. Rules for the CH Insertions. 1.1. CH insertions into PH_3, H_2S, and HCl. The mechanisms for the CH insertions into PH_3, H_2S, and HCl are predicted to be essentially similar to those for the CH insertions into NH_3, H_2O, and HF.[6] These

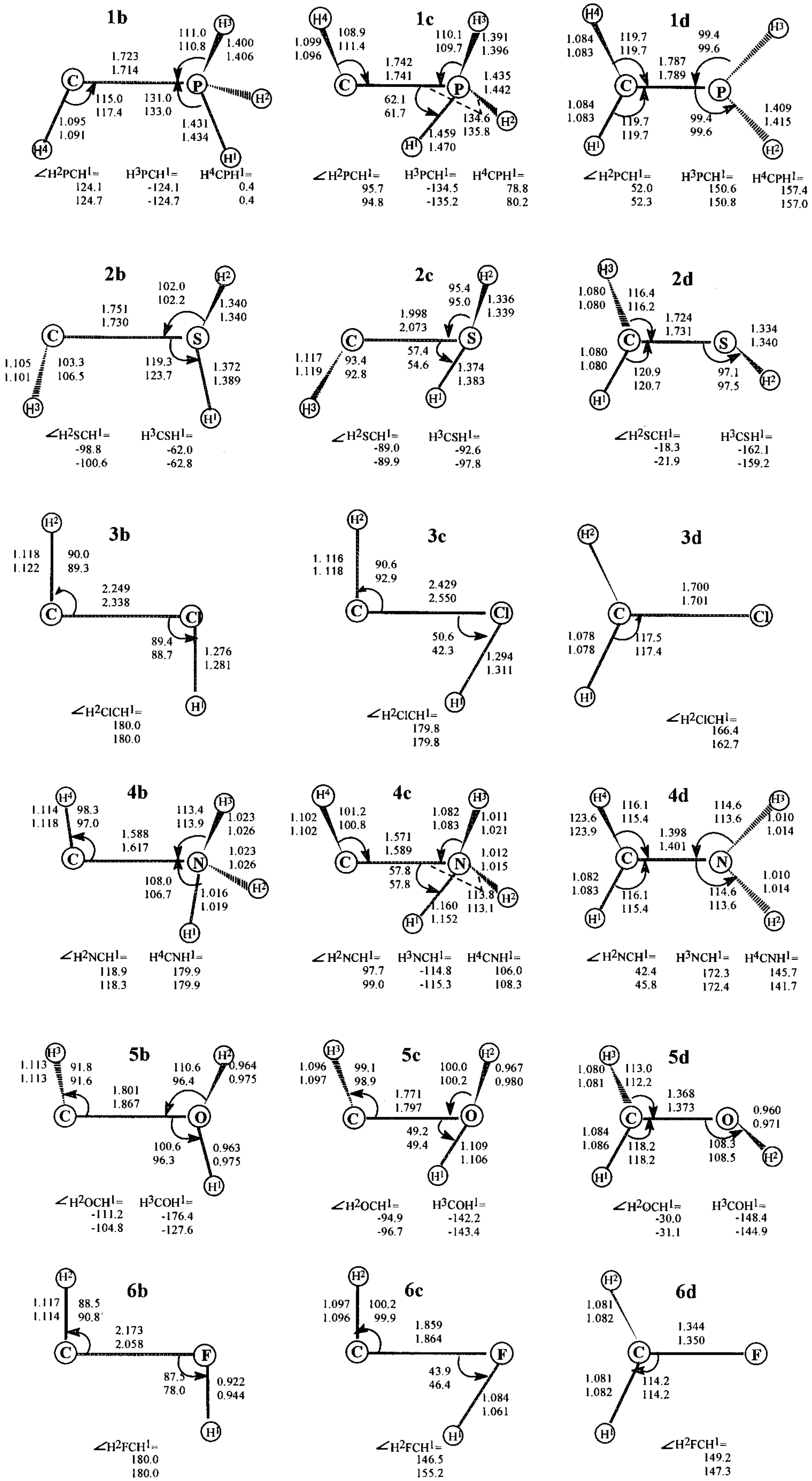

Figure 2. Optimized structures of the intermediate complexes (**mb**), transition states (**mc**), and products (**md**) for the CH insertion reactions with PH_3 (1), H_2S (2), HCl (3), NH_3 (4), H_2O (5), and HF (6). The upper values are the MP2(FC)/6-311++G(d,p) geometric parameters, and the lower values are the MP2(FU)/6-31G(d) ones. Bond lengths are given in angstroms and angles in degrees.

TABLE 1: Relative Energies[a] (kcal/mol) for the Intermediate Complexes, Transition States, and Products of the CH Insertion Reactions with PH_3, H_2S, HCl, NH_3, H_2O, and HF, Together with the (U)MP2/6-311++G(d,p) $\langle S^2 \rangle$ Values, the MP2(FU)/6-31G(d) Zero Point Energies (ZPE, in kcal/mol, Scaled by a Factor of 0.9646), and Imaginary Frequencies (IMG, in cm^{-1}) for the Transition States

		ZPE	IMG	$\langle S^2 \rangle$	MP2/6-311++G(d,p)[b]	MP4/6-311++G(2d,p)[b,c]	G2
CH + PH_3	**1a**	19.2			0.0	0.0	0.0
					(−380.97891)[d]	−381.04587	(−381.09058)
HC−PH_3	**1b**	24.0		0.766	−46.1	−43.7	−47.2
TS	**1c**	22.8	1630.8i		−15.7	−12.6	−16.7
H_2C−PH_2	**1d**	25.2		0.767	−101.8	−96.0	−98.7
CH + H_2S	**2a**	13.6			0.0	0.0	0.0
					(−437.21331)	(−437.28758)	(−437.34257)
HC−SH_2	**2b**	18.4		0.764	−22.8	−22.2	−25.8
TS	**2c**	16.5	1057.5i	0.768	−8.9	−8.6	−10.0
H_2C−SH	**2d**	20.0		0.766	−98.6	−92.9	−95.9
CH + HCl	**3a**	8.3			0.0	0.0	0.0
					(−498.61903)	(−498.69167)	(−498.75231)
HC−ClH	**3b**	10.8		0.777	−2.8	−3.8	−2.9
TS	**3c**	9.5	567.8i	0.798	−1.7	−2.6	−1.6
H_2C−Cl	**3d**	14.4		0.765	−91.8	−86.8	−89.4
CH + NH_3	**4a**	25.4			0.0	0.0	0.0
					(−94.78111)	(−94.84258)	(−94.86997)
HC−NH_3	**4b**	30.6		0.755	−28.1	−25.3	−26.6
TS	**4c**	27.7	1756.5i	0.771	−10.7	−7.0	−8.3
H_2C−NH_2	**4d**	31.4		0.753	−95.5	−90.1	−92.0
CH + H_2O	**5a**	17.1			0.0	0.0	0.0
					(−114.66010)	(−114.71739)	(−114.74419)
HC−OH_2	**5b**	20.8		0.770	−8.5	−8.0	−7.8
TS	**5c**	18.6	1465.8i	0.754	−0.3	−0.0	0.0
H_2C−OH	**5d**	23.3		0.753	−87.0	−84.2	−85.5
CH + HF	**6a**	9.6			0.0	0.0	0.0
					(−138.64448)	(−138.70328)	(−138.76234)
HC−FH	**6b**	12.1		0.869	−1.1	−1.6	−0.2
TS	**6c**	11.6	781.6i	0.762	6.1	3.6	4.4
H_2C−F	**6d**	15.6		0.760	−81.1	−79.7	−81.4

[a] All the relative energies have included the ZPE corrections. [b] The MPn calculations were carried out with the core orbitals frozen and the spin-projected energetic results are used. [c] Single point MP4SDTQ/6-311++G(2d,p)//MP2/6-311++G(d, p) calculations. [d] Values in parentheses are total energies in a.u.

mechanisms are essentially different from that for the CH insertion into H_2[2a] and that for the CH insertion into CH_4.[7] The similarities between the CH and CH_2 insertions into NH_3, H_2O, and HF were discussed in our previous paper.[6]

The binding energies of the initially formed complexes **1b**, **2b**, and **3b** in reactions 1−3 are calculated to be 47.2, 25.8, and 2.9 kcal/mol, respectively, which are comparable to the values 43.4, 22.1, and 3.8 kcal/mol reported previously.[9] The large binding energies of **1b** and **2b** and the "normal" C−P and C−S bond lengths in **1b** and **2b** (1.723 and 1.751 Å, being shorter than or comparable to the C−X bond lengths 1.787 and 1.724 Å in **1d** and **2d**, respectively) imply that **1b** and **2b** are not the simple complexes. The molecular and electronic structures of **1b** and **2b** will be described and discussed in detail in section 2.

The MP2(FU)/6-31G(d) frequency calculations for the transition states **1c**, **2c**, and **3c** predict the (unique) imaginary frequency values of 1630.8i, 1057.5i, and 567.8i cm^{-1}, respectively. In the structures of **1c**, **2c**, and **3c**, the attacked X−H bonds are elongated by only 3.5%, 3.0%, and 1.6% relative to the X−H lengths in the reactants XH_n, respectively. The transition states **1c**, **2c**, and **3c** are predicted to be −16.7, −10.0, and −1.6 kcal/mol lower in energy than their respective reactants **1a**, **2a**, and **3a**, which implies that the CH insertions into PH_3, H_2S, and HCl take place energetically favorably. The barriers (E(**mc**) − E(**mb**)) for the hydrogen-migration processes in reactions 1−3 are calculated to be 30.5, 15.8, and 1.3 kcal/mol, respectively.

The relative energies of the insertion products **1d**, **2d**, and **3d** are −98.7, −95.9, and −89.4 kcal/mol, respectively, which indicates that the CH insertion reactions with PH_3, H_2S, and HCl are all strongly exothermic.

For the structures (see Figure 2) we only mention the predicted C−X bond lengths in the complex, transition state, and product for each of reactions 1−3. The three values are 1.723, 1.742, and 1.787 Å for reaction 1; 1.751, 1.998, and 1.724 Å for reaction 2; and 2.249, 2.429, and 1.700 Å for reaction 3, respectively.

On the basis of the calculated results for reactions 1−3, the following rules can be concluded (referred to as rules A, hereafter). As the X-element moves from left to right (from P to Cl) across the second-row in the periodic table, (i) the binding energy of the complex decreases while the C−X distance in its structure increases, (ii) both the relative energy of the transition state (the height of the overall barrier) and the C−X distance in its structure increase, and (iii) both the reaction enthalpy and the C−X distance in the structure of the insertion product decrease, in contrast to point i.

1.2. Comparison with the CH Insertions into the First-Row Hydrides.

The insertions of CH into NH_3, H_2O, and HF have been previously studied at the MP2(FU)/6-31G(d,p) + ZPEs level.[6] Our present study predicted the same mechanisms for the three reactions. Note that the predicted reaction enthalpy of 85.5 kcal/mol for reaction 5 is very close to the experimental value (86.2 kcal/mol), in contrast to the previous value (93.4 kcal/mol).[6] As shown in Figure 1 the skeletons of energy profiles for the CH insertions into the first- and second-row hydrides are identical ($E(\mathbf{ma}) > E(\mathbf{mb}) < E(\mathbf{mc}) \gg E(\mathbf{md})$). By examining the results for reactions 4−6, it could be found that rules A concluded from the CH insertions into the three second-row hydrides fit completely the CH insertions into the three first-row hydrides. Point ii in rules A indicates that, in the same row, the hydride of the left-hand group is more reactive than the hydride of the right-hand group in these CH insertions.

By comparing reactions 1−3 with reactions 4−6, one could find the following rules (referred to as rules B, hereafter). As the X-element goes from the first- to the second-row in each of the three groups, (i) the binding energy of the complex increases (note that the binding energies of **1b** and **2b** are much larger than those of **4b** and **5b**, respectively), (ii) the relative energy value (overall barrier height) of the transition state decreases and the attacked X−H bond in the structure of the transition state is elongated to a lower extent (the percentages of the elongation decrease from 14.4%−18.3% to 1.6%−3.5%), and (iii) the reaction enthalpy increases. Point ii in rules B indicates that the second-row hydride (X = P, S, and Cl) is more reactive than the corresponding first-row hydride (X = N, O, and F) in these CH insertions.

The most significant difference in the CH insertions between into the first-row hydrides and into the second-row hydrides is that, for each of the reactions 4−6, the C−X bond distances in the complexes, transition states, and products (see Figure 2) decrease monotonically, while the C−X lengths change in disorder for each of reactions 1−3. Comparing **1b** with **4b**, it can be found that atom H^4 is cis to H^1 in **1b**, while in **4b** the two atoms are trans to each other. The difference is also recognized between **2b** and **5b**.

1.3. Comparison with the SiH Insertion Reactions. In our previous theoretical paper[13] the insertions of SiH into NH_3, H_2O, HF, PH_3, H_2S, and HCl were systematically studied, and the skeletons of the energy profiles for these reactions are similar to those (see Figure 1) for the CH insertions ($E(\text{reactants}) > E(\text{complex}) < E(\text{TS}) \gg E(\text{product})$). On the basis of the results calculated at the quite close theoretical level (MP4/6-311++G(2d,p)//MP2/6-311++G(d,p) +ZPEs, see above), the rules A and B concluded from the CH insertions do not fit completely the SiH insertions into the same six hydrides, although the two radicals are valence isoelectronic, and have similar insertion mechanisms. For instance, as the X element moves from left to right across either the first-row or second-row in the periodic table, both the Si−X and C−X bond in the products decrease, but the reaction enthalpy for the SiH insertions increases, while that for the CH insertions decreases; the Si−X bond lengths in the transition states, as well as the relative energy of the transition state for the insertions of SiH into second-row hydrides, do not appear to have the same change trend as found in the CH insertions. As the X-element goes from the first row to the second row in the same group, the reaction enthalpy of the SiH insertions decreases, in contrast to an increase for CH insertions. In addition, the binding energies of complexes in SiH insertions change slightly (not more than 2.0 kcal/mol), while the binding energies of complexes decrease significantly except for the insertions of CH into HF and HCl (as large as about 18.0 kcal/mol). Comparing each of the CH insertions into the hydrides with the corresponding SiH insertion, the relative energy of the transition state for the former is much lower than that for the latter, which indicates that the CH radical is more reactive than SiH toward the same hydrides in inserting.

2. Addition Complexes HC−PH_3 and HC−SH_2. In the following we focus on the complexes. As shown in Table 1 and Figure 1, the complexes HC−PH_3 (**1b**) and HC−SH_2 (**2b**) have very large binding energies and very short X−C bond distances (1.723 and 1.751 Å), which are shorter than or comparable to the X−C bond lengths (1.787 and 1.724 Å) in the products **1d** and **2d**, respectively. The binding energies for **3b**, **5b**, and **6b** are all very small (less than 10 kcal/mol), and they all have very long C−X bond distances compared with those in their respective products. Although the binding energy for **4b** is large (about half of the value for its analogous **1b**), the C−N bond distance (1.558 A) in **4b** is significantly longer than that (1.398 A) in **4d**. It is also noted that the HCX angles in **1b** and **2b** (115.0° and 103.3°, respectively) are significantly larger than 90°, while the HCX angles in the other complexes (see **3b, 4b**, **5b,** and **6b** in Figure 2) are close to 90°. Thus, it may be concluded that **1b** and **2b** are different from the other complexes, which are the loosely bound lone-pair (of the X-atom) donor−acceptor complexes. [6,13]

The P- and S-ylides (H_2CPH_3 and H_2CSH_2) are important reactants in synthetic organic chemistry. As a prototype of ylide the P-ylide has been extensively investigated by theoretical chemists at the various levels, and these studies[14−24] have revealed certain features for its molecular and electronic structure. The P-ylide has a short P−C bond length (1.67−1.68 Å[16−18]), which is much shorter than the P−C single-bond length in $H_3C{-}PH_2$ and close to the P=C double bond length in $H_2C{=}PH$. The P-ylide is several dozens of kcal/mol[15] lower in energy than the separate $^1CH_2 + PH_3$, which indicates a very large binding energy toward $^1CH_2 + PH_3$. The local geometry at the C-center of the P-ylide is not planar and the out-of-plane bending angle is about 30°.[17,18] The electronic structure calculations for the P-ylide indicate a large charge separation at its $P^+{-}C^-$ bond, the (MP2) Mulliken charges[16] being +0.55 and −0.76 e on the P and C atoms, respectively (the natural changes[18] were predicted to be as large as 0.96 and −1.21 e!). In contrast to a pure double ($\sigma + \pi$) bond, the barrier to rotation about the $P^+{-}C^-$ bond in the P-ylide is very low (about 1 kcal/mol or less[16,17,20]). The (MP2) bond order calculations[18] for the P-ylide predict a value of 1.360 for its P−C bond, which is intermediate between the values for the P=C double bond and P−C single bond. In summary, the P-ylide has the following features in its molecular and electronic structure: the short P−C bond length; large binding energy; large charge separation; low internal rotation barrier; intermediate P−C bond order, and the nonplanar local geometry at the C-center. These are considered as the general features in the molecular and electronic structures of ylides.

The P- and S-ylides could be considered as the initially formed complexes in the insertions of methylene into PH_3 and H_2S, respectively (see the relevant energy profiles in ref 15), which stimulate us to realize that the complexes **1b** and **2b** might be similar to the P- and S-ylides in nature although **1b** and **2b** are radicals. In Table 2 listed are the properties of **1b** and **2b**, calculated at the four post-SCF levels, including energetic properties (binding energies, proton-transfer energies (see below), internal rotation barriers, structural properties (the X−C bond lengths and HCX angles), charges, and spin densities, together with dipole moments. As shown in Table 2, the MP2(FU)/6-31G results are significantly different from those calculated at the other levels. We conclude that the d functions contribute greatly to the formation of the special complexes **1b**

TABLE 2: Calculated Properties[a] of $HC-PH_3$ and $HC-SH_2$

	BE[b]	PTE[b]	ΔE_r[b]	$R(X-C)$	∠HCX	charge		spin density[c]		DP[b]
						P	C	P	C	
				$HC-PH_3$						
MP2(FU)/6-31G	21.9	77.6		1.885 (1.857)[d]	108.7	0.445	−0.461	−0.076	1.049	
MP2(FU)/6-31G(d)	43.1	61.1	1.4	1.714 (1.789)	117.1	0.345	−0.501	−0.032	0.979	
MP2(FC)/6-311++G(d,p)	46.1	55.7	0.5	1.723 (1.787)	116.4	0.691	−0.620	−0.081	1.044	3.79
						(0.80)[e]	(−0.793)			
MP4/6-311++G(2d,p)[f]	43.7	52.3	0.2							
G2	47.2	51.5	0.2							
				$HC-SH_2$						
MP2(FU)/6-31G	6.0	82.7		2.256 (1.815)	92.8	0.003	−0.255	−0.052	1.098	
MP2(FU)/6-31G(d)	19.1	83.4	6.4	1.730 (1.728)	106.2	0.156	−0.493	−0.037	1.016	
MP2(FC)/6-311++G(d,p)	22.8	75.8	4.7	1.751 (1.724)	103.3	0.513	−0.660	−0.040	1.038	4.16
						(0.386)	(−0.658)			
MP4/6-311++G(2d,p)	22.2	70.7	7.1							
G2	25.8	70.1	5.2							

[a] Energetic properties in kcal/mol, bond lengths in angstroms, angles in degrees, densities (charges) in electrons, and dipole moments in Deybe. [b] BE, PTE, ΔE_r, and DP denote the binding energy, proton-transfer energy, internal rotation barrier, and dipole moments, respectively. [c] Based on population analyses using MP2 densities. [d] $C-X$ bond lengths in **1d** and **2d**. [e] Natural charges. [f] Calculated at the MP2/6-311++G(d,p) geometries.

and **2b**. It should be pointed out that the exclusion of d functions does not influence the complexes **3b** and **4b** as severely as **1b** and **2b** (not shown in Table 2). In the comparative discussion presented in the next paragraph we will use many published results for the P- and S-ylides that were not calculated at the exactly same levels as those in the present calculations (see Table 2). However, we lay emphasis on finding similarities of the qualitative features between the ylides and complexes **1b** and **2b**.

The proton-transfer energy (PTE) was defined as a criterion of "hypervalency" in ylide by Eades et al.,[20] which is just the energy difference between H_2C-XH_n (ylide) and H_3C-HX_{n-1} (the stable tautomer). In the present study we have defined the PTEs for **mb** (radicals) as the energy differences between **mb** and **md**. The binding energies and proton-transfer energies for the P- and S-ylides can be evaluated on the basis of the energetic results reported in ref 15, which were calculated at the MPn levels with several large basis sets. The evaluated binding energies for the P- and S-ylides are 54−74 and 27−48 kcal/mol, compared with the values 47.2 and 25.8 kcal/mol for **1b** and **2b**, respectively. The evaluated proton-transfer energies for the P- and S-ylides are 53−59 and 73−81 kcal/mol, compared with the values 52.3 and 70.6 kcal/mol for **1b** and **2b**, respectively. The $P-C$ bond length of 1.723 Å (MP2/6-311++G(d,p)) in **1b** is only 0.046 Å longer than the length of 1.677 Å[16,17] (MP2/6-311+G(d,p)) in the P-ylide, and the $S-C$ bond length in **2b** is about 0.1 Å longer than the length (an MP2/6-31G(d) value of 1.635 Å was reported in ref 15) in the S-ylide. The structure of **1b** (see Figure 2) has a symmetry plane in which the $C-H$ bond is cis to the unique $P-H$ bond. The unique $P-H$ bond in **1b** is somewhat shorter than the other two $P-H$ bonds, and the unique HPC angle is significantly larger than the other two HPC angles. It is noted that the P-ylide also has these two geometrical features.[17] The calculated barrier to rotation about the $P-C$ bond in **1b** is extremely low (0.2 kcal/mol) as in the P-ylide (see above). The calculated rotation barrier in **2b** is 5.2 kcal/mol, which is comparable to rotation barriers about normal single bonds (no post-SCF study on the internal rotation in the S-ylide was reported in the literature). Our calculations indicate that **1b** is the only stable rotational conformer of $HC-PH_3$ and **2b** is the only stable conformer of $HC-SH_2$. Population analysis for **1b** and **2b** calculated at the MP2/6-311++G(d,p) level using the MP2 densities indicate that there are considerable charge separations at the $X-C$ bonds as the typical P- and S-ylides. The charges on the P and C atoms in **1b** are +0.691 and −0.620 e, respectively, and the values are +0.513 and −0.660 e on the S and C atoms in **2b**, respectively. The natural charges on the above-mentioned four centers are +0.800, −0.793, +0.386, and −0.658 e, respectively. For the P-ylide the Mulliken population analysis[16] using the MP2/6-31G(d) density predicted the charges of +0.55 and −0.76 e on the P- and C-centers, respectively, which are slightly larger than the MP2(FU)/6-31G(d) charges (see Table 2) on the corresponding centers in **1b.** For the radicals **1b** and **2b**, our bond order calculations using the natural analysis as well as using the "atom-in-molecule" methods were not successful or gave apparently unbelievable results. The calculated spin densities on the X and C centers in **1b** and **2b** (see Table 2) imply that the unpaired electron predominately resides on the C center in each of the two radicals.

The binding energy value of **1b** is larger than that of **2b**, and the proton-transfer energy value of **1b** is smaller than that of **2b**. Both facts imply that **1b** is more stable than **2b**. The HCP angle (115.0°) in **1b** deviates to a greater extent from 90° than the HCS angle (103.3°) in **2b**.

The above descriptions and comparative discussions indicate that **1b** and **2b** have several ylidic features and they are "ylide-like radicals". Since **1b** and **2b**, as the reaction intermediates, are much lower in energy than their respective reactants and (proton-transfer) transition states (see Figure 1), they might be observed experimentally. We report the calculated dipole moments of **1b** and **2b** in Table 2. The calculated (at the (U)MP2/6-311++G(d,p) level) isotropic hyperfine coupling constants for the hydrogen atoms (see Figure 2) in the two radicals are $a(H^1) = -6.6$ G, $a(H^2) = 34.4$ G, $a(H^3) = 34.4$ G, and $a(H^4) = -20.7$ G in **1b** and $a(H^1) = 0.7$ G, $a(H^2) = 34.1$ G, and $a(H^3) = -16.3$ G in **2b**. To our knowledge, there have been no experiments to study the insertions of CH into PH_3 and H_2S, and we hope that people are able to find their usefulness in synthetic chemistry as the P- and S-ylides.

The bonding nature in **1b** and **2b** (ylide-like radicals) was not investigated in the present study, and the investigation should be based on a complete understanding of the bonding nature in ylides. The bonding nature in the P-ylide was investigated in many papers[16,18,19,22−24] for at least 20 years, and in the latest paper[16] the authors claimed that no new principle (e.g., hypervalency or ylidic bonding) was needed. At the present stage we presumably believe that the P^+-C^- bond in the P-ylide has the partial double bond character and, also, the ionic interaction has an important contribution to the bonding. However, the important thing is that the complexes HC−PH_3 and HC−SH_2 have been realized to be different in nature from the donor−acceptor complexes HC−NH_3 and HC−OH_2 for which the binding[6] is simply due to the interaction between the empty p-orbital of CH and the lone-pair orbital of the X atom (X = N or O). It is noted that, on the basis of their frontier MO arguments, Naito et al.[18]gave a simple and clear explanation for the fact that H_2CPH_3 is the most stable ylide whereas H_2CNH_3 is actually not an ylidic species.

Conclusion

The insertions of CH into NH_3, H_2O, HF, PH_3, H_2S, and HCl have been systematically studied at the MP4/6-311++G(2d,p)//MP2/6-311++G(d,p) + ZPE and G2 levels, which indicate the six insertions all take place through an initially formed intermediate complex followed by a hydrogen-migration process via a transition state leading to the product. The insertion mechanisms are similar to those for the insertions of SiH into the six hydrides (previously studied). According to the movement of the X element in hydrides across the same row or the same group in the periodic table, two three-point sets of rules (rules A and rules B; see section 1.1 and 1.2 for details) are found. We conclude for the same row hydrides, the reactivity of left-hand hydride toward CH is higher than that of right-hand hydrides, and for the same group hydrides, the reactivity of above hydrides is higher than that of below ones. However, the rules A and B do not fit completely the insertions of SiH into the same hydrides, although CH and SiH are valence isoelectronic and have similar mechanisms. By comparison of the insertions of CH with SiH ones, it is found that the CH radical is more reactive than SiH.

Interestingly, the complexes HC−PH_3 and HC−SH_2 are not the simple (loosely bound) donor−acceptor complexes as formed in the insertions of CH into the other hydrides and in the insertions of SiH into the six hydrides. The investigations on their molecular and electronic structures reveal that they have the following features: very short central bond lengths (1.723 and 1.751 Å) that are shorter than or comparable to the bond lengths in the products (1.787 and 1.724 Å), respectively; large binding energies (47.3 and 25.8 kcal/mol, respectively); considerable charge separations at the central bonds; and low internal rotation barriers around the central bonds. On the basis of detailed comparison with the qualitative features of the typical ylides, the radicals HC−PH_3 and HC−SH_2 are considered to be similar to the ylides in nature, being “ylide-like radicals”. Since HC−PH_3 and HC−SH_2 exist in deep wells in the energy surfaces, we proposed they might be observed experimentally. The calculated dipole moments and hyperfine coupling constants for these two radicals are reported.

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