Ylide-like addition complexes in insertion reactions of CH with PH_3 and H_2S

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The intermediate addition complexes HC–PH_3 and HC–SH_2 formed in the CH insertion reactions with PH_3 and H_2S have large binding energies and short central bond lengths, exhibiting 'ylidic' features in their molecular and electronic structures.

We previously studied the CH insertion reactions with NH_3, H_2O and HF by means of *ab initio* calculations[1] and found intermediate addition complexes existing prior to the transition states in the reaction paths. The reaction paths for these reactions are illustrated by eqns. (4)–(6) where the reactants,

$$\begin{array}{ccccccc} CH + XH_n & \rightarrow & HC\text{–}XH_n & \rightarrow & TS & \rightarrow & H_2CXH_{n-1} \\ \mathbf{ma} & & \mathbf{mb} & & \mathbf{mc} & & \mathbf{md} \end{array}$$

(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, $n = 1$

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 or 6), respectively, and the energy profiles have the following skeletons: E (**ma**) > E (**mb**) < E (**mc**) $\gg$ E (**md**).

Recently we performed *ab initio* calculations for the CH insertion reactions with PH_3, H_2S and HCl. These reactions have similar reaction paths [illustrated by eqns. (1)–(3), respectively] and similar skeletons of the energy profiles to those for reactions (4)–(6). However, we have found that the intermediate addition complexes HC–PH_3 **1b** and HC–SH_2 **2b** initially formed in reactions (1) and (2) are not the simple complexes,[1] but are similar in nature to the phosphonium and sulfonium ylides (P- and S-ylides).

Standard *ab initio* molecular calculations were performed by using the Gaussian 94 W suite of programs.[2] The structures of reactants, intermediate complexes, transition states, and products were optimized at the (U)MP2(FC)/6-31G(d) and (U)MP2(FC)/6-311++G(d,p) levels. Frequency calculations were carried out at the (U)MP2(FC)/6-31G(d) level to characterize stationary points and to evaluate zero-point energies (ZPEs). Finally single-point (U)MP4SDTQ(FC)/6-311++G(2d,p)//(U)MP2(FC)/6-311++G(d,p) calculations were performed. For open-shell systems the $<S^2>$ values are all <0.8. We recalculated the insertion paths for reactions (4)–(6) at these levels and obtained similar results to those reported in ref. 1. The MP4SDTQ/6-311++G(2d,p)//MP2/6-311++G(d,p) energetic results (the spin-projected ones for the open-shell systems) corrected with the (MP2/6-31G(d)) ZPEs and the MP2/6-311++G(d,p) geometrical results are used unless otherwise noted.

The potential energy curves in Fig. 1 represent the calculated insertion reaction paths for reactions (1)–(3). The relative energies of **mb**, **mc** and **md** and the structures of **mb** (m = 1–3) are shown in Fig. 1. The term 'relative energy' (of a species) in the present article means the energy of a species relative to the reactants in the same reaction.

The binding energies of the intermediate addition complexes **1b**, **2b** and **3b** in reactions (1)–(3) are 43.4, 22.1 and 3.8 kcal mol^{-1} (1 cal = 4.184 J) respectively. The negative relative

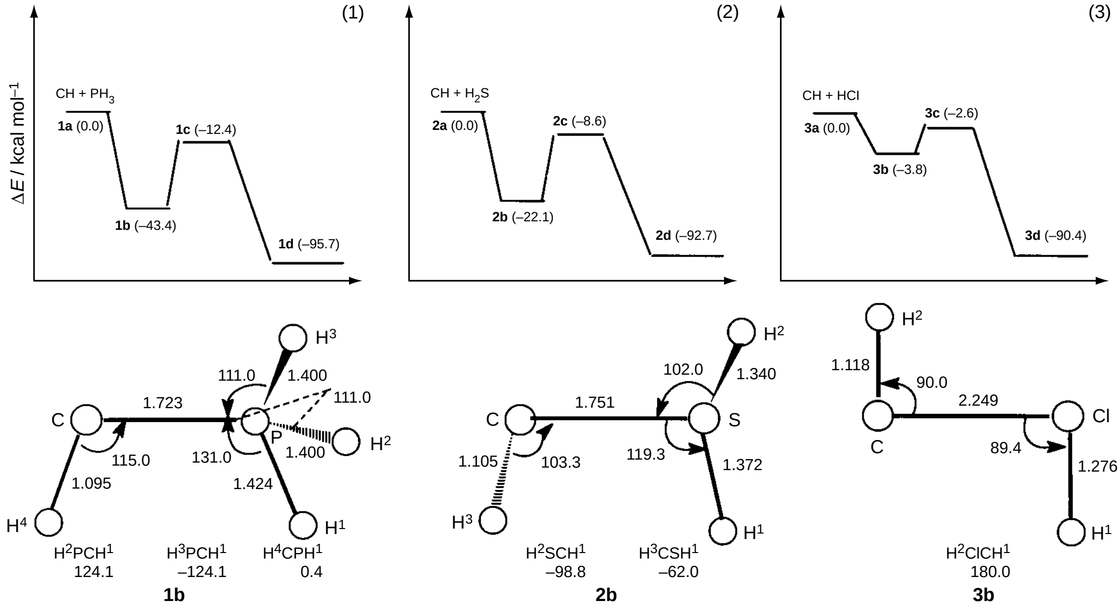

Fig. 1 A schematic diagram of the potential energy curves of the CH insertion reactions with PH_3 (1), H_2S (2) and HCl (3) with the MP4SDTQ/6-311++G(2d,p)//MP2/6-311++G(d,p) relative energies in kcal mol^{-1} [corrected with the MP2/6-31G(d) ZPEs] in parentheses. In the lower part of the figure are the MP2/6-311++G(d,p) structures of the intermediate addition complexes **mb** (m = 1–3) formed in the three insertion reactions (bond lengths in Å and angles in °).

Table 1 Binding energies (E_b) and the C–X bond distances (R) of the addition complexes HC–XH_n

	HC–PH_3 **1b**	HC–SH_2 **2b**	HC–ClH **3b**	HC–NH_3 **4b**	HC–OH_2 **5b**	HC–FH **6b**
E_b[a]/kcal mol^{-1}	43.4[b]	22.1[b]	3.8	24.9	7.9	1.5
R(C–X)[c]/Å	1.723	1.751	2.249	1.588	1.801	2.173
	(1.787)[d]	(1.724)	(1.700)	(1.398)	(1.368)	(1.344)

[a] The MP4SDTQ/6-311++G(2d,p)//MP2/6-311++G(d,p) + ZPE energetic results. [b] After the (MP4) BSSE corrections, these two values (the E_b values for **1b** and **2b**) are reduced by 3.4 and 3.4 kcal mol^{-1}, respectively. [c] Optimized at the MP2/6-311++G(d,p) level. [d] Values in parentheses are the C–X bond lengths in the respective insertion products.

Table 2 Calculated properties of HC–PH_3 and HC–SH_2

	E_{pt}[a]/ kcal mol^{-1}	ΔE[a]/ kcal mol^{-1}	H–C–X[b]/°	Q(C)[b]/e	Q(X)[b]/e
HC–PH_3 **1b**	52.3	0.2	115.0	−0.620	0.691
HC–SH_2 **2b**	70.6	7.1	103.3	−0.660	0.513

[a] E_{pt} and ΔE denote the proton-transfer energy and internal rotation barrier, respectively, calculated at the MP4SDTQ/6-311++G(2d,p)//MP2/6-311++G(d,p) + ZPE level. [b] H–C–X and Q (the charge on atomic centers) are predicted at the MP2/6-311++G(d,p) level.

energy values of the transition states **1c**, **2c** and **3c** (−12.4, −8.6 and −2.6 kcal mol^{-1}, respectively) and the large negative relative energy values of the insertion products **1d**, **2d** and **3d** (−95.7, −92.7 and −90.4 kcal mol^{-1}, respectively) indicate that the CH insertion reactions with PH_3, H_2S and HCl are all feasible and strongly exothermic.

In the following we focus on the addition complexes. Table 1 lists the binding energies and the C–X bond distances of the intermediate addition complexes **mb** (m = 1–6), together with the C–X bond lengths of the insertion products (**md**). As shown in Table 1, **1b** (HC–PH_3) and **2b** (HC–SH_2) have very large binding energies and very short C–X bond distances (1.723 and 1.751 Å, respectively) which are shorter than or comparable with the C–X bond lengths (1.787 and 1.724 Å) in **1d** and **2d**, respectively. The binding energies for **3b**, **5b** and **6b** are all very small (< 10 kcal mol^{-1}), and they all have very long C–X bond distances compared with those in their respective insertion products. Although the binding energy for **4b** is quite large (about half the value for its analogue **1b**), the C–N bond distance (1.588 Å) in **4b** is significantly longer than that (1.398 Å) 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 (also see ref. 1) are close to 90°. It is 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.[1]

The P- and S-ylides (H_2CPH_3 and H_2CSH_2) are important reactants in synthetic organic chemistry. In our previous studies,[1,3] we already noticed that the $^1CH_2$ insertion reactions into hydrides have similar reaction paths and similar energy profile skeletons to those for the CH insertion reactions. The P- and S-ylides could be considered as the intermediate addition complexes in the $^1CH_2$ insertion reactions with PH_3 and H_2S, respectively (see ref. 7), and it is natural to infer that the CH addition complexes **1b** and **2b** are similar to the P- and S-ylides (although **1b** and **2b** are radicals). As a prototype of ylides the P-ylide has been extensively investigated by quantum chemists[4–8] (its bonding nature is still being explored[4]), and the following features are known. The P-ylide has a short C–P bond length[4–6] (shorter than the length in $H_3C–PH_2$) and very large binding energy towards $^1CH_2 + PH_3$. There is a large charge separation at its C^-P^+ bond[4,6,8] and the rotational barrier about this bond is extremely low.[4,5,8] These features are considered as general features in the molecular and electronic structures of ylides.

Table 2 lists the calculated properties of **1b** and **2b**. The proton-transfer energy[8] (E_{pt}) is defined as a criterion of 'hypervalency' in ylides, and we have defined the E_{pt} values for **mb** as the energy differences between **mb** and **md**. The binding energies and E_{pt} values for the P- and S-ylides can be evaluated based on the energetic results reported in ref. 7 which were calculated at the MP levels comparable to those in the present study. The large binding energies for **1b** and **2b** (43.4 and 22.1 kcal mol^{-1}, respectively) are somewhat smaller than those for the P- and S-ylides (54–74 and 27–48 kcal mol^{-1}, respectively). The E_{pt} values for **1b** and **2b** are 52.3 and 70.6 kcal mol^{-1}, respectively, which are comparable with those for the P- and S-ylides (53–59 and 73–81 kcal mol^{-1}, respectively). The C–P bond length in **1b** is only 0.046 Å longer than the length of 1.677 Å[4,5] [at the MP2/6-311+G(d,p) level] in the P-ylide, and the C–S bond length in **2b** is about 0.1 Å longer than the length [1.635 Å[7] at the MP2/6-31G(d) level] in the S-ylide. The MP2 Mulliken charges on the C and P atoms in **1b** are −0.620 and +0.691, respectively (the MP2 charges of −0.76 and +0.55 for the P-ylide were reported in ref. 4) and the charges on the C and S atoms in **2b** are −0.660 and +0.513, respectively, which implies considerable charge separations in **1b** and **2b**. The rotational barrier in **1b** is extremely low (0.2 kcal mol^{-1}) as in the P-ylide (*ca.* 1 kcal mol^{-1} or less[4,5]), and the barrier in **2b** is 7.1 kcal mol^{-1} (no reported post-SCF results for the barrier in the S-ylide are available).

1b and **2b** are not loosely bound complexes and they have ylidic features in their molecular and electronic structures. Since **1b** and **2b** exist in deep minima in the potential energy surfaces (Fig. 1), they might be observed in some experiments (spectroscopy, EPR, *etc*). We would expect the ylide-like radicals **1b** and **2b** to be useful in synthetic chemistry as are the P- and S-ylides.

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Notes and References

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