From Carbene and Phosphine to Ylide. A Symmetry-Breaking Allowed Pathway

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Abstract: Nonempirical pseudopotential SCF calculations have been performed on the $PH_3 + CH_2\ (^1A_1) \rightarrow PH_3CH_2$ reaction, using a double ζ (+ d orbitals on the phosphorus) basis set. The calculated properties of the methylenephosphorane molecule are in perfect agreement with previous all-electron ab initio calculations. The heat of reaction is 44 kcal/mol. A very large barrier (>35 kcal/mol) prohibits the direct addition if the P and CH_2 atoms are maintained in the same plane as suggested by the ylide equilibrium geometry. If the CH_2 plane is perpendicular to the phosphorus lone pair, the barrier disappears; then a sudden rocking of the methylene group, occurring at short P-C distances, leads monotonically to the ylide potential well. The generality of such a symmetry-breaking mechanism is discussed.

Introduction

Phosphonium ylides are generally synthesized through the action of a strong base on a phosphonium halide:

$$R_3P^+CH_3X^- \xrightarrow{\text{base}} [R_3P{=}CH_2 \leftrightarrow R_3P^+{-}{}^-CH_2] + HX$$

However, a direct synthesis of Wittig compound from carbene addition on phosphine has been reported in the early 1960s.[1]

$$(C_6H_5)_3P\!: + :CCl_2 \rightarrow (C_6H_5)_3P{=}CCl_2$$

This reaction may seem rather strange from only chemical intuition since the lone pairs directed along the PC axis should repel the reactants. The present work shows through accurate quantum-mechanical calculations on model compounds PH_3 and CH_2 that a direct coplanar attack is actually prohibited by a large barrier, but that a barrierless pathway may be found when the carbene presents its vacant $2p_z(C)$ atomic orbital in front of the phosphorus lone pair. The calculations have been performed at a double ζ ab initio level including a set of d orbitals on the phosphorus. The core electrons are replaced by a monoelectronic nonempirical pseudopotential determined according to the method of Durand and Barthelat,[2] and introduced by Daudey[3] in the HONDO algorithm.[4] The reliability of the pseudopotential techniques is now well established and is exemplified in section I through a systematic comparison of the methylenephosphorane properties with previous all-electron ab initio calculations. The details of the optimized basis set and of the parameters of the pseudopotential are available upon request.

I. Structure of Methylenephosphorane

The final product PH_3CH_2 has been extensively studied through several ab initio calculations[5-9] (for semiempirical calculations see ref 10, 11, and 19). Absar and Van Wazer[5] calculated two conformations only in a rather large Gaussian basis set. The most extensive calculations have been performed by Lischka,[7] who optimized the geometry using several basis sets. The largest basis (basis no. 5 of ref 7) was of triple ζ quality plus polarization functions on all atoms. The calculation also included correlation effects to analyze the rotational properties around the PC bond.

Another double ζ (+ d on the phosphorus atom) SCF calculation has been recently published by Strich.[9] Our basis set compares with the valence basis set of Strich and basis no. 3 of Lischka. It therefore should give comparable results as far as the pseudopotentials do not introduce any artifact.

Our optimized geometry is compared with those given by Lischka and Strich in Table I, together with the force constant of the P-C bond. It appears that our geometry is in overall excellent agreement with the ab initio results. The most relevant experiments concern Me_3PCH_2; electron diffraction[12] gives $R(\text{P-C}) = 1.64$ Å and $\angle CPC = 101.6°$, and infrared studies[13] give $k_{\text{P-C}} = 5.59$ mdyn/Å.

A much-debated point concerns the pyramidalization of the strongly negative carbon atom. The Lischka's largest basis set suggests a 10° pyramidalization with an extremely small minimum (0.07 kcal/mol), while Strich stresses the planarity of the carbon atom in his calculation. Our optimum β value is intermediate but the whole discussion about planarity must be relativized if one remembers (see Figure 1) that the energy changes under a 10° pyramidalization are smaller than 0.2 kcal/mol in all calculations. The essential point is not the planarity or nonplanarity of this carbon atom but the flatness of the potential hole, suggesting that a nonsymmetrical perturbation (for instance, substitution on the phosphorus atom) may give a significant deviation from planarity.

In agreement with previous calculations,[5,7,9] the rotational barrier around the PC bond is negligible; the staggered conformation is only favored by 0.007 kcal over the eclipsed one. The charge repartition is not reported here since it closely follows the detailed atomic population analysis given by Lischka, supporting an essentially ionic $H_3P^+\text{-}CH_2^-$ picture. This electronic distribution suggests the stabilizing role of π electronic acceptor substituents, such as conjugated systems, on the carbon atom.

The participation of the d orbitals is the same as in ab initio calculations; the Mulliken atomic population analysis gives 0.16 e in the d_{xz} atomic orbital (0.14 e in ref 7), which essentially results from the delocalization from the $2p_z$ "lone pair" of the carbon atom. This "lone pair" also delocalizes into the PH bonds through hyperconjugation. Both effects contribute to a small π bond order and to planarity.

The nonempirical pseudopotentials appear once again as a reliable technique. As a further proof, Table II gives the valence molecular orbital SCF energies.

II. The $PH_3{=}CH_2 \rightleftarrows PH_3 + CH_2$ Reaction

The energy of the reaction has been calculated through a geometry optimization of the PH_3 and the singlet $^1A_1$ state of CH_2. Their calculated geometries are given in Table III, together with experimental values. The ground state of CH_2 is of $^3B_1$ character, but it is well known that most of the chemically important carbenes are substituted and have a singlet ground state;[16] this is especially true for $:CCl_2$ involved in the observed reaction.[1] This energy[34] of reaction—44 kcal/mol—is very large. It may be defined as the $P^+\text{-}C^-$ bond en-

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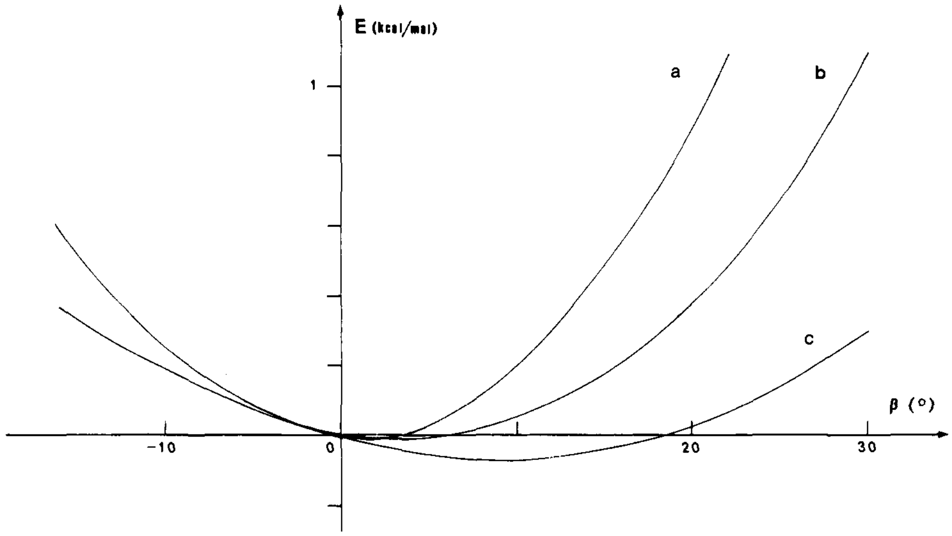


Figure 1. H_3PCH_2 energy variation under pyramidalization of the carbon atom: (a) ref 9; (b) this work; (c) ref 7.

Table I. Optimized Geometry of H_3PCH_2[a]

ref	P-C, Å	P-H, Å	C-H, Å	∠HCH, deg	∠HPH, deg	β, deg	$k_{P\text{-}C}$, mdyn/Å
Lischka[7]	1.67	1.40	1.07	121	99.8	10	5.90
Strich[9]	1.64	1.40	1.08	118.5	98.8	1.5	
this work	1.682	1.421	1.081	118.9	99.8	3.7	5.67

[a] β is defined in Figure 2.

Table II. Valence Molecular Orbital Energies of H_3PCH_2

	Strich,[9] eV	this work, eV
5a′	−7.54	−7.39
2a″	−13.90	−13.94
4a′	−14.61	−14.49
3a′	−15.59	−15.47
1a″	−16.27	−16.14
2a′	−21.85	−21.86
1a′	−26.67	−26.51

ergy of the ylide. This value is about ⅔ of the reported P-C bond energy in phosphines (63-65 kcal/mol[17,18]). The ⅔ ratio seems reasonable since the bond strength should become lower when increasing the phosphorus coordinance. This is anyway a more reliable value than the CNDO prediction[19] (1 eV without d orbitals, 10 eV when including d orbitals, the role of d orbitals in CNDO calculations being dramatically overestimated). The question arises as to whether the $PH_3 + CH_2$ reaction will present an activation barrier, despite the large energy stabilization of the final product. The analysis of correlation diagrams for the most natural pathway (simple breaking of the P-C bond of the ylide without rotation of the fragments) suggests that the reaction is forbidden by the orbital correspondence: the crucial plane of symmetry is not the bisector plane P_1 of the CH_2 group, but the PCH_2 plane (plane of symmetry for the eclipsed conformation if not the perfect plane of symmetry for the degenerate staggered conformation).

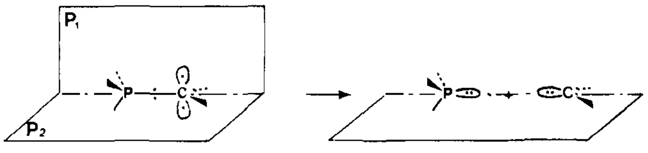
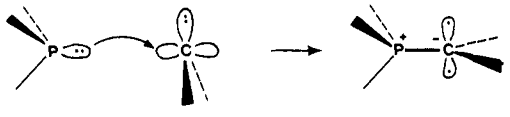


Table III. Optimized Geometries of PH_3 and Singlet CH_2

	PH_3 (C_{3v})		$^1A_1CH_2$	
	PH, Å	HPH, deg	CH, Å	HCH, deg
optimized geometries (this work)	1.424	95.0	1.112	105.0
expt	1.42	93.8	1.11	102.4
ref	14		15	

This plane defines a σ P-C orbital and a π "lone pair" on the carbon atom (slightly delocalized by hyperconjugation tails on the PH bonds. In the final products the four corresponding electrons belong to two σ lone pairs (Figure 3). In terms of states the correspondence diagrams (Figure 4) correlate the ground state of the ylide with the $(\sigma^2 \rightarrow \pi^2)$ $^1A_1$ CH_2 doubly excited state, as noticed by Ostoja Starzewski and Bock,[19] and the singlet ground state of the $PH_3 + CH_2$ system correlates with the $(\sigma^2\sigma^{*2})$ doubly excited state of the ylide. An energy barrier is expected for the thermal reaction, while the photochemical reaction from the lowest singlet excited state of the carbene would be allowed.

With such a large energy difference between the initial and final products, the occurrence of an energy barrier seems somewhat unlikely. It is clear that no barrier has to occur if the phosphorus lone pair may delocalize into the π vacant b_1 ($2p_z$) molecular orbital of the singlet carbene. To do so, it is sufficient to bring the methylene molecule in a plane perpendicular to the direction of the phosphorus lone pair. In such a case the



only plane of symmetry is the P_1 plane, and the four important electrons remain in symmetrical MOs all along the reaction

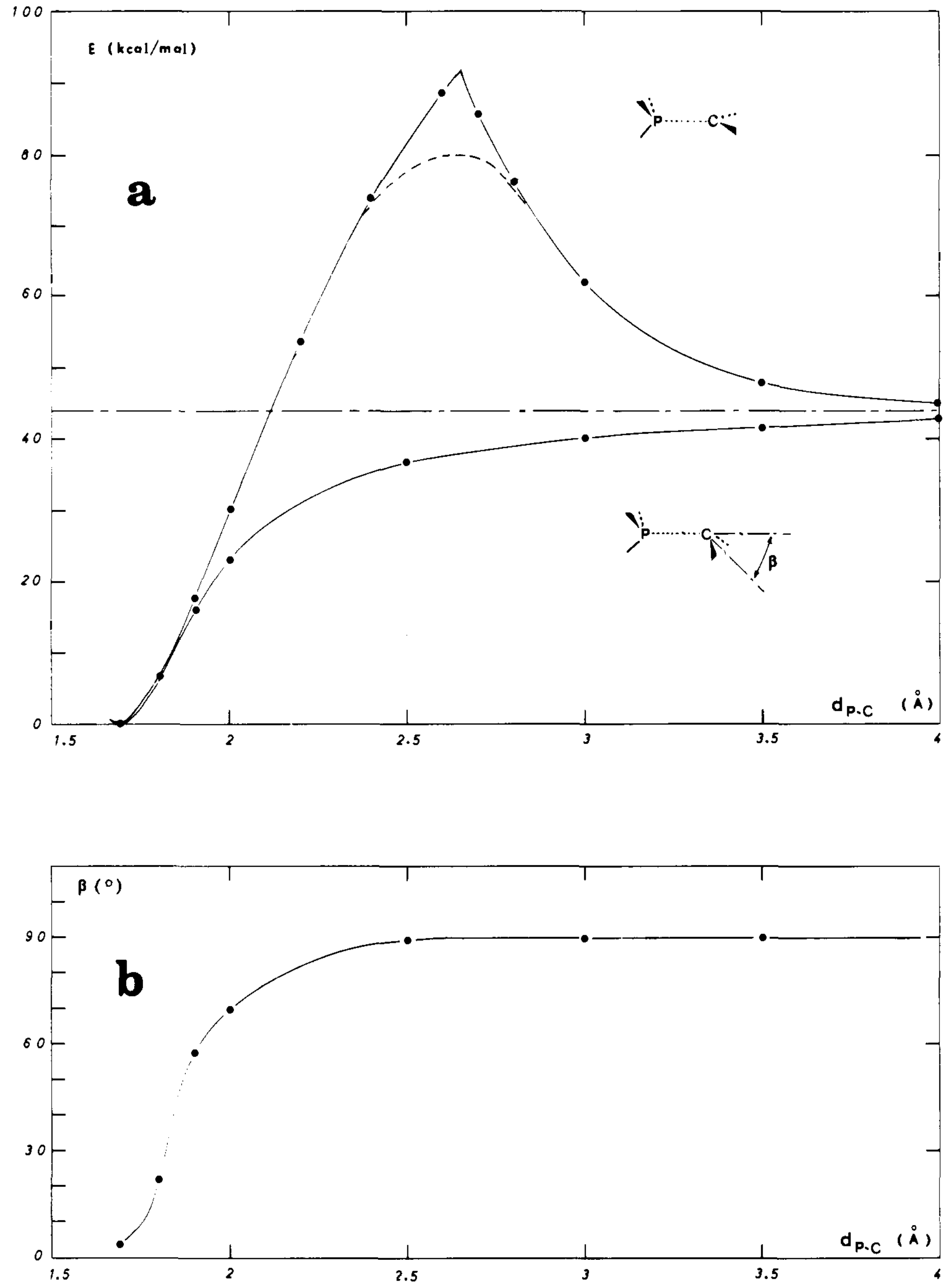


Figure 2. (a) Potential curves for the $H_3PCH_2 \rightleftharpoons PH_3 + CH_2\ (^1A_1)$ reaction. Upper curve: coplanar approach. Lower curve: after optimization of β. (b) Variation of the β pyramidalization angle along the optimized pathway.

path. The reaction becomes allowed if one follows a reaction path in which the CH_2 molecule offers its vacant $2p_z$ orbital to the σ lone pair of its partner, before progressively rotating its two CH bonds up to planarity. For intermediate distances, the stabilizing factor is a $n(P) \rightarrow 2p_z(C)$ electronic delocalization, i.e., a $PH_3 \rightarrow CH_2$ charge transfer.

Once this possibility is noticed, the only question remains quantitative; it concerns the progressivity or the suddenness of the rotation of the CH_2 fragment as a function of the P-C distance. Numerical calculations are required to answer this question.

Bond Formation without Rotation. The planar breaking of the P-C bond has been explored from both sides, starting from either the phosphorus ylide or final products geometries of the fragments which are not very different anyway (see Tables I and III). The two curves increase and cross at about a 2.6-Å P-C distance at energies $\simeq$45 kcal/mol (see Figure 2) above the separated fragments energy. The actual barrier after geometry optimization and correlation corrections would be somewhat lower (>35 kcal/mol) but the reaction is strongly forbidden.

Bond Formation with Rocking of the Fragments. For a few interatomic P-C distances the β rocking angle (see its definition in Figure 2) of the CH_2 group has been optimized, showing clearly (see Figure 2) that (a) no activation barrier occurs once the geometry is relaxed; (b) the rocking angle varies rapidly at short distances (Figure 2b). Its value is still 69° at R_{PC} = 2 Å, 58° at R_{PC} = 1.9 Å, and falls down to 20° at R_{PC} = 1.8 Å. This rapid variation of β between 0 and 69° for a 0.22-Å bond lengthening must be related to the flatness of the potential curve $E = f(\beta)$ around the equilibrium geometry (see Figure 1).

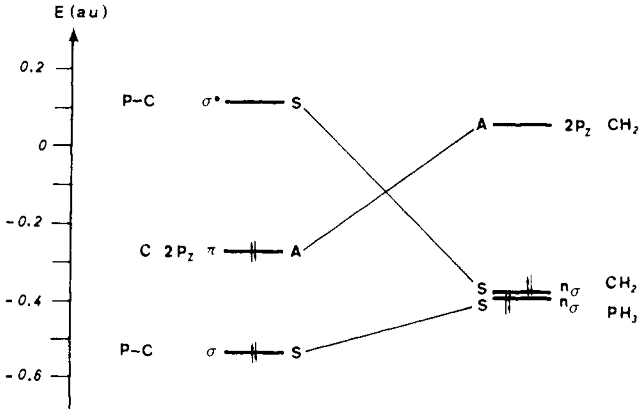


Figure 3. Orbital correlation diagram for the $H_3P{=}CH_2 \rightleftharpoons H_3P + CH_2$ reaction.

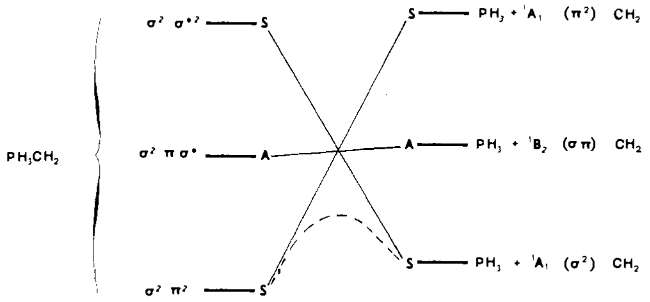


Figure 4. State correlation diagram for the $H_3P{=}CH_2 \rightleftharpoons H_3P + CH_2$ reaction.

Conclusions

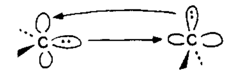
Our stereomechanism for the addition of a carbene on a phosphine may be supported by the structure of a germanium analogue, namely, the so-called "complex of germanium dichloride with triphenylphosphine".[20] The P-Ge bond is a covalent σ bond (2.5 Å) but the germanium center remains strongly pyramidal, offering its vacant 4p$_z$ AO to the phosphorus lone pair, as occurs at our intermediate distances. The germanium atom does not tend to become planar, as does the carbon atom, since the two electrons of the lone pair prefer to keep their s character. This difference of behavior between C and Ge is linked to the largest energy difference between s and p orbitals in Ge (which also appears in the geometries of singlet CH_2 (HCH = 102.4[15]) and GeH_2 (HGeH = 92.6°[21]).

The studied reaction is a further example of the possibility of allowing apparently forbidden reactions by a departure from the symmetry suggested by the final state geometry. In the same field of carbene chemistry, one may quote the addition of carbene to ethylene to yield cyclopropane, which is forbidden for a symmetrical approach of the singlet carbene and becomes allowed by removal of the symmetry, as noticed by Hoffmann[22] and verified by Dewar et al. through MINDO calculations[23] and Kutzelnigg et al. through accurate ab initio calculations.[24]

A closer example of such non-least-motion paths is the dimerization of singlet carbenes, many times theoretically

$$R_2C: + :CR_2 \rightarrow R_2C{=}CR_2$$

studied,[25-29] which will be forbidden for a coplanar attack and allowed when a lone pair delocalizes in a vacant orbital of the partner to give the σ bond, while the other pair builds the π bond. The dimerization of triplet carbenes is experimentally known[30] but it is of course symmetry allowed.[30,31] The observation of the singlet state dimerization is made difficult by the high reactivity of singlet carbenes, which prevents a sufficient concentration. Finally, one can mention in this field recent theoretical studies on reaction of singlet methylene with the hydrogen molecule.[32,33]



Acknowledgment. The authors wish to thank Dr. R. Wolf and his co-workers, Dr. P. Rivière, and Professor A. Lattes for helpful discussions.

References and Notes

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(34) To get the enthalpy of the reaction, the zero-point energy difference must be taken into account. An estimation of this difference from IR data gives $\frac{1}{2}h\nu_{P-C} \approx 8$ kcal/mol, so that $\Delta H \approx 36$ kcal/mol.