Inorg. Chem. **1987**, *26*, 1799–1805 **1799**

Contribution from the Laboratoire de Physico-Chimie Moléculaire, UA 474,
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Ab Initio CI Study of Chemical Reactions of Singlet Phosphinidene

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Received July 22, 1986

The potential energy surfaces for the addition and insertion reactions of phosphinidene with ethylene have been characterized by using ab initio molecular orbital theory including electron correlation. Detailed comparison is made among the structures of phosphirane, vinylphosphine, and their phosphaalkene isomers. The main interconversion barriers between these systems were evaluated.

Introduction

The chemistry of electron-deficient species has been extensively investigated for the past several years both experimentally and theoretically. Most investigations dealt first with carbenes, followed later by silylenes and nitrenes. Theoretical analyses of structure and reactivity, primarily addition[1-8] and insertion reactions,[9-17] have pointed out certain analogies but also differences among these systems.

Phosphinidenes, however, the phosphorus analogues, have only recently been characterized as complexed entities and identified by chemical trapping.[18] This explains why relatively few data are currently available on the reactivity of phosphinidene, in particular toward the ethylene group, a basic substrate extensively examined with the other electron-deficient species.

To our knowledge, no theoretical approach to this problem has yet been undertaken. We thus began examining the modes of approach of a singlet phosphinidene onto an olefin, leading to either phosphirane by addition, a system already synthesized, or vinylphosphine by insertion, of which only substituted derivatives have so far been isolated.

In parallel to these two reaction products, we also examined their isomer, phosphaalkene monomethylated on carbon, and evaluated the interconversion barriers of these different systems.

Computational Details

The calculations were performed with the MONSTERGAUSS[19] program. The split-valence 4-31G basis set was used, augmented by one set of d polarization functions on phosphorus ($\zeta_P{}^d = 0.57$).[20]

The molecular geometries were fully optimized at a SCF level with respect to all bond lengths and bond angles by the Broyden–Fletcher–Goldfard–Shanno gradient method.[21] The detection of transition states was carried out by employing the Powell algorithm.[22] The stationary points were characterized by force constant analysis (number of negative eigenvalues). For the maxima a zero gradient (accuracy 10^{-3}) has been obtained.

The effect of electron correlation at these optimized geometries was estimated by configuration interaction employing the CIPSI algorithm.[23] A variational zeroth-order wave function is built from an iterative selection of the most important determinants, the other ones being taken into account through a second-order Möller–Plesset type perturbation expansion.

Addition Reaction of Singlet Phosphinidene with C_2H_4

In the series of three-membered saturated rings, work has begun to be devoted to the phosphirane ring only recently. A general pathway for obtaining complexed phosphiranes was recently proposed by Mathey et al.[24] Until the present, however, phosphirane has not been synthesized by the direct cycloaddition of a phosphinidene on an alkene, contrary to what is observed in the nitrogen series when aziridine is obtained. In order to understand more fully the origin of this problem, we undertook the theoretical analysis of this addition reaction.

As is known from the isoelectronic nitrene (NH), phosphinidene (PH) is characterized by a triplet ground state[25] and the lowest energy singlet state is described as a biradical with two degenerated orbitals of p character, each occupied by one electron; the n_σ pair is strongly coupled with the P–H bond and participates at deeper energies. Thus singlet phosphinidene is not similar in its electronic structure to a singlet carbene (frontier orbitals not degenerate).

In the analysis of the addition mechanism on ethylene, we chose as reaction coordinate the distance *d* separating the phosphorus atom from the middle of the C–C bond (Figure 1). Preliminary calculations showed that the preferential approach was in the plane bisecting the $\pi_{C=C}$ bond, with local C_s symmetry (Figure 1).

The SCF results in Table I show that there is a monotonically lowered energy change between the initial state and the final state, with an exothermicity of 293 kJ·mol^{-1}. It should be noted that even though there is no activation energy involved, energy decreases notably only when the reactants are closer than the sum of the van der Waals radii. Analysis of the results after configuration interaction (CI) does not modify these conclusions. The potential energy curve is practically parallel to that obtained at the SCF level. The energy decrease between the initial and final

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Table I. Variations in Geometry and Energy as Functions of the Distance *d* for the Addition of PH to C_2H_4

	d, Å						
	1.687[a]	2	2.5	3	3.5	4.5	5.5
r, Å	1.504	1.420	1.349	1.327	1.319	1.316	1.315
l, Å	1.407	1.409	1.415	1.416	1.416	1.419	1.419
C_1–P_3, Å	1.844	2.123	2.589	3.072	3.56	4.55	5.54
α^2, deg	96.47	91.12	86.08	86.18	87.16	87.18	87.15
β_1, deg	117.62	119.91	121.74	122.02	122.05	122.10	122.12
β_2, deg	112.60	115.05	116.10	115.92	115.90	115.79	115.75
E_{SCF}, hartrees	−18.855818	−418.828025	−418.777432	−418.758984	−418.750564	−418.744968	−418.744705
E_{CI}, hartrees	−419.165339	−419.137701	−419.083452	−419.063502	−419.054069	−419.046760	−419.046701

[a] Phosphirane.

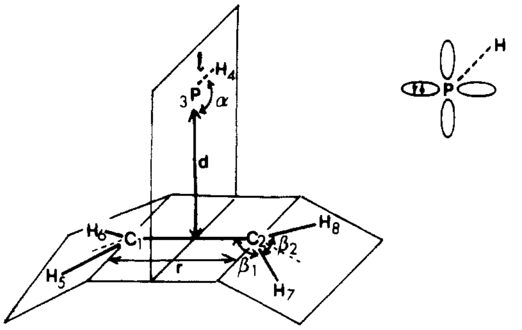

Figure 1. Internal coordinates used for the cycloaddition of PH to C_2H_4.

states is 311.2 kJ·mol^{-1}. As a result of interactions we observe after CI that a distance of 4.5 Å is sufficient to show a significant splitting between the energies associated with the two closed-shell configurations corresponding to an occupation by two electrons of each p orbital of phosphinidene. This energy splitting between these two states increases rapidly with the lowering of *d*. Thus a SCF CI approximation appears correct to investigate the addition mechanism.

The analysis of changes in geometric parameters (Table I) and the Mulliken populations (Figure 2) along the reaction path enabled us to determine that preferential approach initially gives rise to a primary interaction between the vacant p orbital of phosphinidene and the occupied $\pi_{C=C}$ of ethylene. This is reflected by a charge transfer from the olefin toward phosphinidene, which plays the role of acceptor. This electrophilic phase continues until around *d* = 2.5 Å. The nucleophilic phase, characterized by transfer in the opposite direction, from phosphinidene toward ethylene, appears only at the end of the reaction path and coincides with the considerable energy drop observed. The primary interaction that then occurs involves the occupied p orbital of phosphinidene and $\pi^*_{C=C}$ of ethylene. This leads to the creation of P–C bonds and also to the elongation of the C–C bond, via the occupation of the $\pi^*_{C=C}$ orbital. Thus, for *d* = 2 Å and in comparison to *d* = 2.5 Å (Figure 2), the net charge of phosphorus passes from negative to positive, with a steady and simultaneous decrease of the population index of the C–C bond and a substantial increase of that of the P–C bonds.

As is the case for the cycloaddition of carbene on ethylene,[1,2] we observe an initial "π type" approach. Nevertheless, the subsequent progression of the mechanism no longer requires a pivoting movement of the system to permit the formation of σ ring bonds via the participation of the n_σ pair. In this case, it occurs naturally as a result of the presence of an occupied and fully available p pair. In this context, the situation of phosphinidene is to be compared to those observed in the addition of sulfur[26] and nitrene[8]

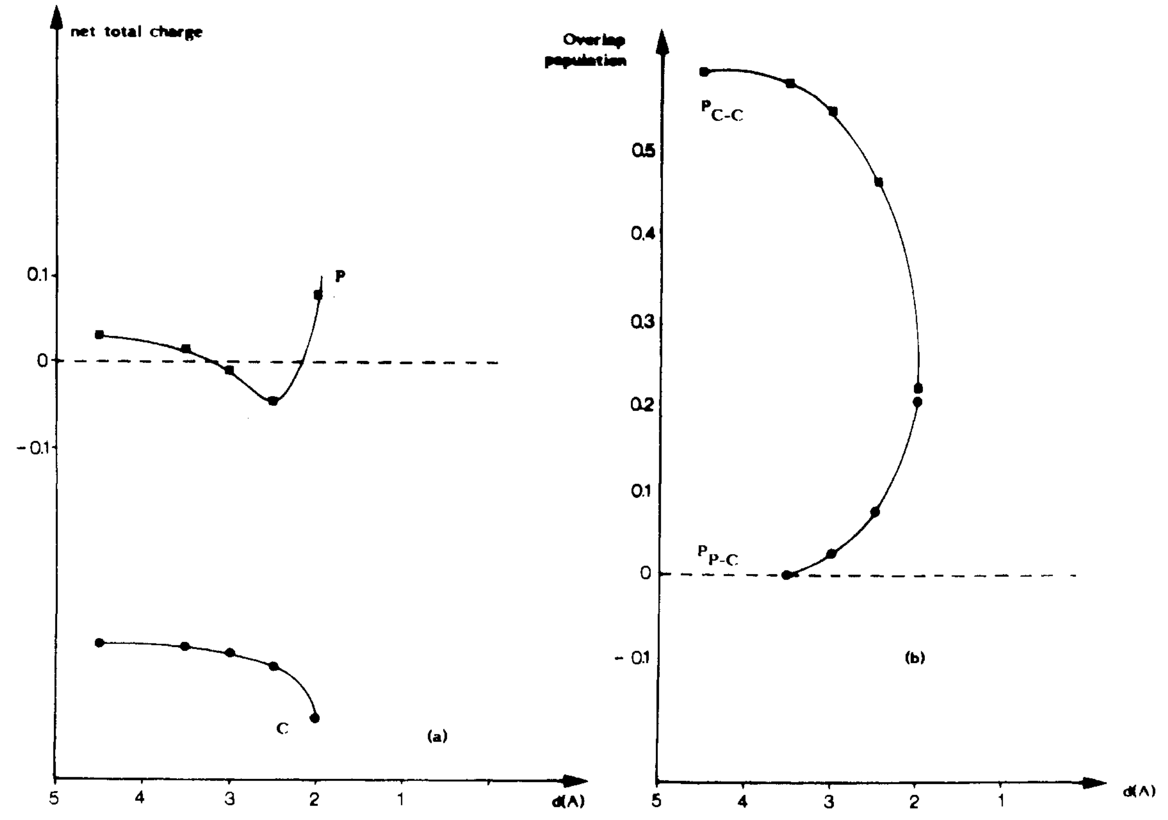

Figure 2. Variations in net total charges (a) and overlap populations (b) along the addition reaction path.

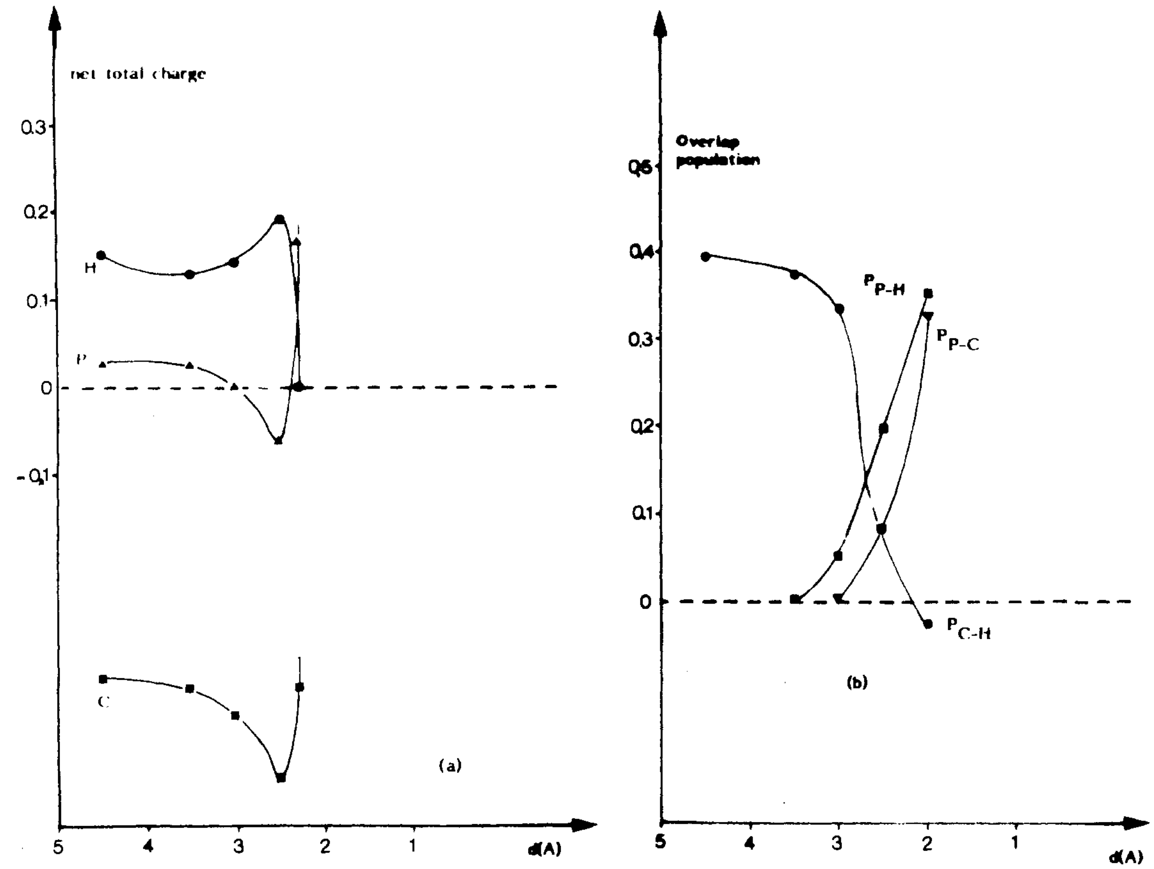

Figure 3. Variations in net total charges (a) and overlap populations (b) along the insertion reaction path.

on ethylene.

The results obtained thus demonstrate a typical example of an orbital-symmetry-allowed process along a least-motion path requiring no activation energy. This possibility of forming two bonds in a concerted stereospecific addition leading to phosphirane is related to the lifting of the initial degeneracy of the two p orbitals of phosphinidene and to the occupation of the orbital of appropriate symmetry.

In the case of complexed phosphinidenes, the only entities thus far identified, we have shown[25] that the occupied orbital of phosphorus with p character was involved in a bond with the metal atom, thereby placing us in a situation similar to that of singlet carbenes. When complexed phosphinidenes are cycloadded to olefins, we expect the mechanism to have a concerted character, analogous to that of singlet carbenes. These comments agree with those formulated on the bases of experimental findings, in light of the retention of olefin stereochemistry during the condensation, and the results observed with conjugated dienes.[24]

To conclude this part of the analysis, it would appear that the obstacle to obtaining phosphirane by direct reaction of singlet phosphinidenes on olefins is more in the difficulty in generating singlet phosphinidene than in the actual reaction mechanism.

Insertion Reaction of Singlet Phosphinidene with a C–H Bond

Insertion reactions of carbenes in H–H and C–H bonds have been extensively studied in the past several years.[9-14] On the basis of the results gathered, it is clearly established that these insertions occur in a concerted non-least-motion manner with no barrier. The mechanisms suggested in the first theoretical studies were of the abstraction/recombination type,[9] while recent calculations seem to suggest the more rapid formation of a three-center bond.[12,13] More recently, the examination of similar reactions with silylenes[15,16] has indicated the same type of mechanisms with non-nil activation barriers, especially in the case of insertion in C–H bonds.

Very little experimental work has been carried out with phosphinidenes. A recent study,[27] however, has led to the development of a method for the insertion of a complexed phosphinidene in a carbonyl-activated C–H bond. We have undertaken the analysis of the insertion of singlet phosphinidene in the C–H bond of an ethylene compound, in order to elucidate the mechanism leading to vinylphosphine.

After preliminary studies, we chose as reaction coordinate the distance d between the phosphorus atom and a point on the C–C bond located 1 Å from C_1, with all other geometric parameters being optimized. The calculations showed that only phosphinidene approach with the phosphorus atom in the plane of ethylene could lead to an insertion in the C–H bond. An initial position of phosphorus out of the ethylene plane obligatorily proceeded to an addition reaction.

Under these conditions, the energy changes along the reaction pathway (Table II) show the existence of a transition state that we were able to characterize as being associated with a single negative eigenvalue. Energy changes decreased rapidly after the transition state. The barrier obtained at the SCF level is 49.74 kJ·mol^{-1}. Calculations performed with CI on the structures optimized at the SCF level led to a barrier reduction of 25.5 kJ·mol^{-1} but not to its disappearance. We also note that a distance around d = 4 Å is sufficient to show a significant splitting between the energies associated with the two closed-shell configurations corresponding to an occupation by two electrons of each p orbital of phosphinidene; thus a SCF + CI treatment appears correct to analyze this insertion mechanism.

Modifications of geometric parameters have enabled us to conclude on a concerted mechanism. The C–H bond of ethylene breaks concomitantly with the formation of P–C and P–H bonds, the transition state appearing as a three-center structure. This concerted character is also seen in the analysis of Mulliken populations (Figure 3) carried out at points along the reaction path. We see the decrease in the overlap population index of the

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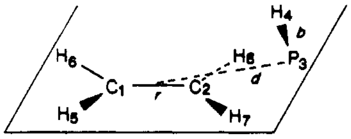
Table II. Variations in Geometry and Energy as Functions of the Distance *d* for the Insertion of PH into the C–H Bond of C_2H_4



	d, Å						
	2.016^a	2.3	transition state (2.496)	3	3.5	4.5	5.5
r, Å	1.320	1.350	1.311	1.309	1.315	1.317	1.317
l, Å	1.407	1.400	1.410	1.413	1.414	1.416	1.418
C_2–H_8, Å	2.455	2.630	1.216	1.082	1.079	1.073	1.072
P_3–H_8, Å	1.407	1.395	1.548	2.003	2.420	3.320	4.330
P_3–C_2, Å	1.830	2.045	2.240	2.720	3.200	4.200	5.216
$\angle P_3H_8C_2$, deg	47.63	50.40	107.64	120.38	128.24	151	155
$\angle H_4P_3C_2$, deg	97.77	94.80	86.56	84.73	86.50	88.17	88.34
E_{SCF}, hartrees	−418.860 55	−418.842 83	−418.725 912	−418.741 787	−418.744 71	−418.744 802	−418.744 850
E_{CI}, hartrees	−419.164 91		−419.037 005				−419.046 812

[a] Vinylphosphine.

C–H bond and the simultaneous increase in those of the P–H and P–C bonds (Figure 3).

It should also be noted that phosphinidene approaches out of the plane of the hydrogen atom in order to favor the two essential interactions involved in the insertion process. One involves the vacant p orbital of PH and the σ_{C-H} orbital of ethylene; the other involves the occupied p orbital of phosphinidene and the σ^*_{C-H} orbital. These two interactions lead to charge transfers in opposite directions. The first predominated during the electrophilic phase at the beginning of the reaction pathway up to the transition state. The second, with a back-transfer, where the phosphorus atom reacts as a donor, takes the system into the second phase of the reaction and terminates at the definitive cleavage of the C–H bond. In light of these results, any modification of the phosphinidene system that leads to an increase in its electrophilic character (position of the vacant p orbital) should facilitate the insertion reaction.

This two-phase mechanism is the same type as those characterized in the insertion reactions of carbenes and silylenes into the C–H bonds.[7,14] This analogy is also found in the concerted character of the approach. In the case of the insertion examined, the results obtained lead to the conclusion of a passage via a three-center bond with rupture and simultaneous formation of bonds and not an abstraction/recombination.

Phosphirane, Vinylphosphine, and Phosphaalkenes

In parallel to the analysis of addition and insertion mechanisms, we undertook a more detailed examination of the products formed at the end of the reaction: phosphirane, vinylphosphine and their isomers, phosphaalkenes monomethylated on carbon and on phosphorus.

The examination of energies associated with the structures minimized at the SCF level (Figure 4) shows that vinylphosphine is the energetically favored compound, phosphaalkene monomethylated on carbon being the least stable isomer. Because of the presence of a saturated ring and three acyclic derivatives with a π system, however, it was important to perform CI calculations, since electron correlation effects could be different for these three systems. The most important corrections were observed for phosphaalkenes and phosphirane, leading to a different order of stability after CI. Phosphaalkene methylated on phosphorus thus appears as the energetically favored entity, while vinylphosphine is the least favored of the four systems. Even though the energy differences are low, it is noteworthy that the order obtained is not in disagreement with experimental data on these systems. Phosphaalkenes are the best known systems experimentally so $CH_3P{=}CH_2$ has been recently identified by SPE.[28] In contrast the low yields obtained when attempting to synthesize primary or secondary vinylphosphines show their intrinsic instability.[29]

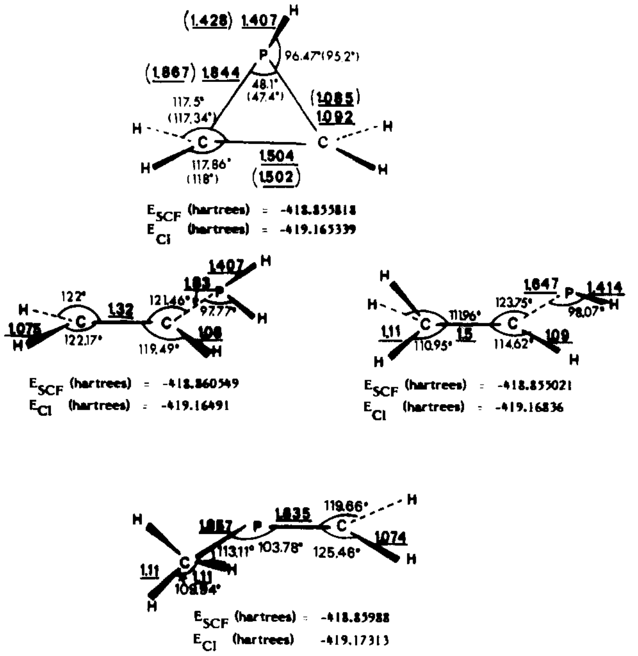


Figure 4. Geometries for phosphirane, vinylphosphine, and phosphaalkenes. Optimized and experimental (in parentheses) bond lengths are in Å.

Electronic and Structural Characteristics. $HP{=}CHCH_3$ and $CH_3P{=}CH_2$. Theoretical work has been devoted to $HP{=}CH_2$ during the last several years,[30-34] which has enabled this system to be structurally characterized. Several planar conformations of the methylated derivatives were a priori possible, corresponding to staggered or eclipsed positions of the methyl group in relation to the P=C double bond, but also in relation to the phosphorus pair.

For the phosphaalkene monomethylated on carbon the total energy values obtained after optimizing geometric parameters at the SCF level show that conformations **1** and **2** are more stable than **3** and **4** (Figure 5). The trans isomer is the energetically favored entity. We thus encounter the results obtained for other systems of this type that may be interpreted on the basis of the interaction balance between the $\pi_{P=C}$ and $\pi^*_{P=C}$ orbitals on one

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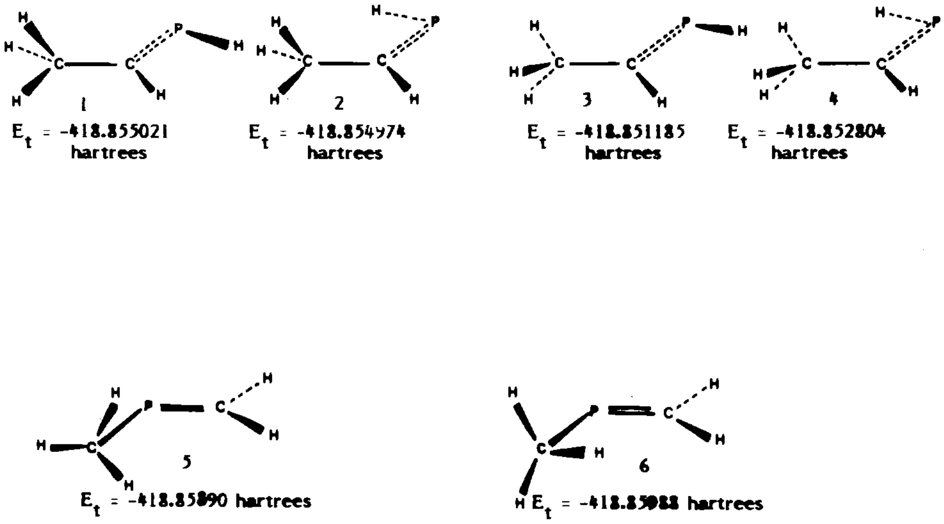

Figure 5. Conformations of $HP{=}CHCH_3$ and $CH_3P{=}CH_2$.

hand and the π_{Me} and π^*_{Me} orbitals on the other hand.[34,35] Similarly for the phosphaalkene methylated on phosphorus, the methyl group adopts conformation **6**, in which one of its CH's eclipses the P=C bond (Figure 5).

In terms of the geometric parameters, the results obtained for the methylated derivatives show only minimal differences in comparison to those for the unsubstituted derivative, which we examined in a prior study with an identical basis set.[31] The main parameters remain practically unchanged and are close to experimental values.[36]

The examination of the Mulliken populations (Figure 6) shows an overall $P^+–C^-$ polarity that is attenuated for the phosphaalkene monomethylated on carbon and accentuated for the one methylated on phosphorus in comparison to the case for the unsubstituted derivative ($Q_P = +0.23$, $Q_C = -0.60$). The π-electron distribution, on the other hand, is always characterized by a quasi-symmetry ($HP{=}CHCH_3$, $Q_P^\pi = -0.08$, $Q_C^\pi = +0.02$; $CH_3P{=}CH_2$, $Q_P^\pi = +0.02$, $Q_C^\pi = -0.09$), which has enabled us to interpret certain aspects of the reactivity of these systems. Finally, we may note that the participation of d orbitals at the level of phosphorus is weak since it is 0.21 and 0.23 e for $HP{=}CHCH_3$ and $CH_3P{=}CH_2$ with preferential participation of d orbitals with σ symmetry. This participation is manifested primarily at the levels of molecular orbitals characteristic of the σ_{P-C} and σ_{P-H} bonds.

Phosphirane. Various theoretical studies[37-41] of phosphirane have been carried out, but all have been performed on the basis of the experimentally determined structure or with optimization to a semiempirical level. The geometric parameters (Figure 4) that we have determined are in good agreement with those obtained with microwave studies,[42,43] reflecting ring tension. In particular, there is a low phosphorus angle of 48.1° for an experimental value of 47.4° and very long P–C bonds. In addition, the ∠ HPC angle of 96.47°, close to the value of 95.2° obtained with microwaves, shows the considerable pyramidalization of phosphorus and the pronounced s character of the lone pair of this atom. As has been noted,[42] we also observed a repulsion between cis P–H and C–H groups, shown by a $P–H_{cis}$ distance greater than $P–H_{trans}$.

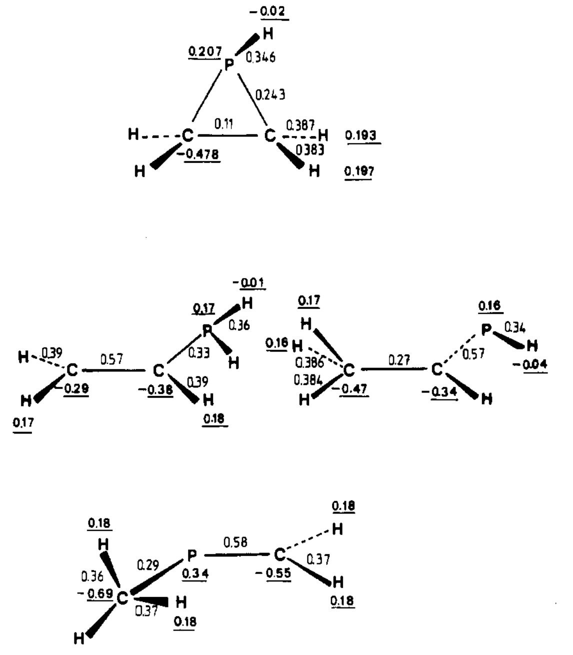

Figure 6. Mulliken populations: net total charges (underlined) and overlap populations.

The phosphorus atom in this entity has a net positive charge, +0.207 higher than in phosphaalkene, while the carbon atoms are more negative. The d orbitals of phosphorus have a slightly greater participation than in phosphaalkene, since their total population is 0.24 e. As already suggested for these three-membered saturated rings, we have observed the existence of p–d interactions between the π,π* orbitals of ethylene and the phosphorus d orbitals with adequate symmetry. Even though these interactions are weak, they are added to those of σ delocalization to explain the stability of the ring. We have formulated similar comments in a prior study of phosphirene.[44] We also note the low population indices of the P–C and C–C bonds in comparison to those obtained for single bonds of the same type (Figure 6), that of the C–C bond reflecting the occupation of $\pi^*_{C=C}$, given the occupied pair interaction of P–H ↔ $\pi^*_{C=C}$. This fragility of the P–C bonds can be compared

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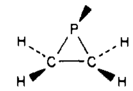
Table III. Frontier Orbitals of Phosphirane, Vinylphosphine, and Phosphaalkenes

		$H_2P—CH=CH_2$		$HP=CH—CH_3$		$CH_3P=CH_2$	
orbital	energy, eV	orbital	energy, eV	orbital	energy, eV	orbital	energy, eV
$\sigma^*_{P—C}$	5.19	$\pi^*_{C=C}$	4.30	$\pi^*_{P=C}$	2.94	$\pi^*_{P=C}$	2.9
n_P	9.85	n_P	9.81	$\pi_{P=C}$	9.11	$\pi_{P=C}$	9.29
$\sigma_{P—C}$	10.31	$\pi_{C=C}$	10.32	n_P	10.26	n_P	9.92
$\sigma_{C—C}$, $\sigma_{P—H}$	12.33	$\sigma_{C—C}$, $\sigma_{P—H}$	12.87	$\sigma_{P—C}$, $\sigma_{P—H}$	13.22	$\sigma_{P—C}$	13.21
$\sigma_{C—H}$	13.88	π_{PH_2}	14.25	$\sigma_{C—H}$	14.37	$\sigma_{C—H}$	15.14

to experimental observations of ring-opening reactions.[24b]

Vinylphosphine. To our knowledge, no theoretical study has been performed on the insertion product, vinylphosphine. Among the various configurations possible posing the problem of an interaction between the lone pair of phosphorus and the $\pi_{C=C}$ system, that of minimum energy apparently corresponds to a syn structure. This structure is characterized by a total absence of $n_P \leftrightarrow \pi_{C=C}$ conjugation with an especially long P–C bond and considerable pyramidalization of phosphorus (Figure 4). This atom has a net charge of +0.17, on the same order as in the phosphaalkene isomer (Figure 6), the participation of the d orbitals of 0.25 e being slightly greater. In the syn structure, the d orbitals with π symmetry are responsible for this increased participation, primarily at the level of π_{PH_2}. The carbon bearing the greatest net negative charge is that bound to phosphorus. A complementary analysis of the conformations of this system is current in progress with photoelectron spectroscopy data.[45]

The analysis of the frontier orbitals of the four systems (Table III) shows that the lone pair of phosphorus has the lowest energy in phosphaalkenes. In phosphirane and vinylphosphine, however, the energy positions are very close, consistent with both entities having similar degrees of nucleophilicity. Associated with $\pi^*_{P=C}$ the first virtual orbital of phosphaalkenes with a notable localization on the phosphorus, however, is much lower than those of phosphirane and vinylphosphine, where it corresponds respectively to $\sigma^*_{P—C}$ and $\pi_{C=C}$. We may also note the considerable localization of this first virtual orbital on the phosphorus of phosphirane.

Interconversion Mechanisms. After characterizing phosphirane, vinylphosphine, and phosphaalkenes by similar energy values, we examined the main interconversion mechanisms at the SCF level, implying the determination of transition states, which could be unambiguously determined with the process explained earlier (associated with a single negative eigenvalue in the force constant matrix). As one starts from the saddle point structure and follows the intrinsic reaction coordinate, it has been demonstrated that the transition states lie on pathways connecting the reactants to the products.

Phosphirane–Vinylphosphine. After the existence of a barrier for the insertion reaction and an addition reaction with no activation barrier were shown it was possible to pose the problem of the formation of vinylphosphine as an insertion reaction product or one resulting from the isomerization of phosphirane.

The search for a transition state, whose electronic and structural characteristics are given in Figure 7, led to a high barrier for this mechanism at 417.6 kJ·mol^{-1}. This high value is related to the substantial electronic destabilization of phosphirane following the breaking of a P–C bond, which is not compensated by simultaneous gain at the level of nuclear repulsion. this is reflected by a σ_{P-C} HOMO highly destabilized in the transition state (−6.81 eV). The energy position of the phosphorus pair, however, is practically unchanged (−9.3 eV).

Geometrically speaking, this saddle point with a 2.006-Å P–C bond is closer to vinylphosphine than to the phosphirane ring (Figure 7). The 1.318-Å C–C bond also reveals a double bond, since the two carbons are perfectly sp^2. The 1,2-migration occurs via a three-center bond, with P–H and C–H lengths of 1.587 and 1.246 Å and associated overlap populations of 0.127 and 0.106.

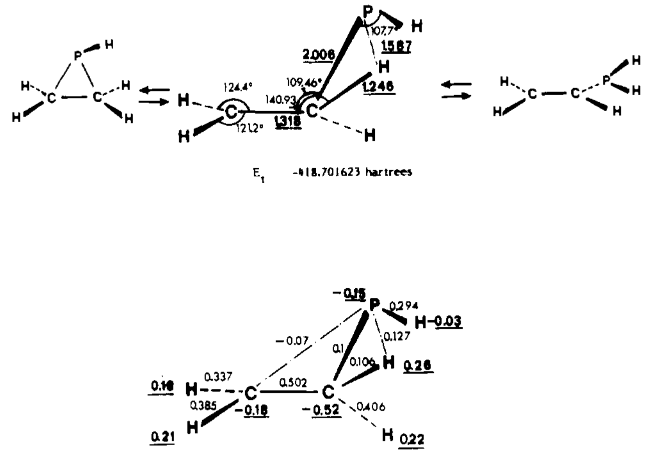


Figure 7. (Top) Transition-state geometry for the interconversion phosphirane–vinylphosphine (bond distances in Å). (Bottom) Mulliken populations: net total charges (underlined) and overlap populations.

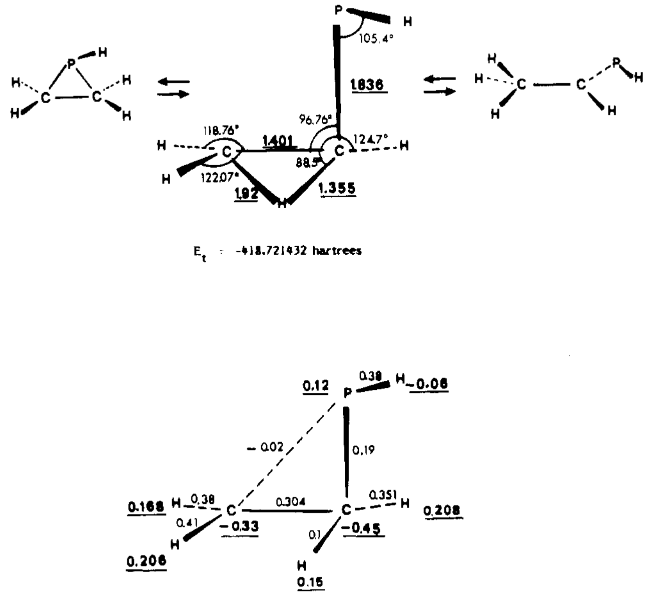


Figure 8. (Top) Transition-state geometry for the interconversion phosphirane–HP=CHCH$_3$ (bond distances in Å). (Bottom) Mulliken populations: net total charges (underlined) and overlap populations.

These results are to be compared to those obtained by Pople et al.[46] in their theoretical analysis of 1,2-migrations, where well-bridged transition states were determined. We may also note the net negative charge of phosphorus, resulting from charge accumulation on this atom after the rupture of the P–C bond.

Phosphirane–HP=CHCH$_3$. The analysis of the phosphirane ↔ HP=CHCH$_3$ interconversion led to a lower barrier than above, at 352.4 kJ·mol^{-1}, but which nevertheless remained high.

As shown by the geometric parameters in Figures 4 and 8, the transition state corresponds to a structure that is intermediate

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[45] Lacombe, S.; Gonbeau, D.; Pfister-Guillouzo, G., to be submitted for publication.

[46] Pople, J. A.; Raghavachari, K.; Frisch, M. J.; Binkley, J. S.; Schleyer, P. V. *J. Am. Chem. Soc.* **1983**, *105*, 6389.

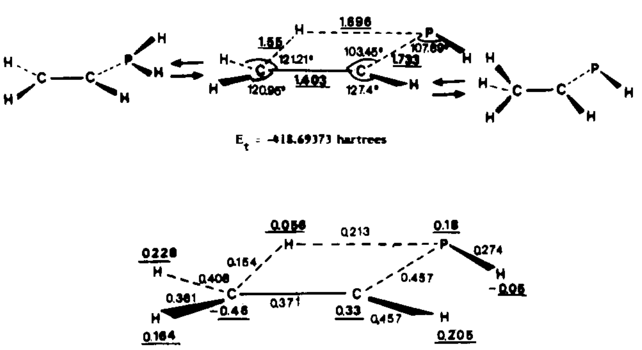

Figure 9. (Top) Transition-state geometry for the interconversion HP=CHCH$_3$–vinylphosphine. (Bottom) Mulliken populations: net total charges (underlined) and overlap populations.

between phosphirane and phosphaalkene. Although one of the P–C lengths is partially broken, the other presents a single-bond character 1.836 Å long and an overlap population of 0.19, very far from the value of 0.57 of the P=C double bond in HP=CHCH$_3$. In addition, the 1,2-migration that occurs leads to hydrogen bridging between the two carbons in the transition state, since the two C–H bond lengths are 1.355 and 1.92 Å.

Phosphirane–CH$_3$P=CH$_2$. The phosphirane ↔ CH$_3$P=CH$_2$ interconversion mechanism corresponds to a scission of the C–C bond and a migration of the hydrogen bound to phosphorus.

The SCF calculations performed allow us to consider probably a two-step mechanism beginning with a scission of the C–C bond followed by formation of a ring-opened intermediate. Further insight into this mechanism may be obtained by examination of this structure, and we cannot account for this properly within an SCF approximation. No further attempt has been made because experimentally the opening of the phosphirane ring has been observed to occur with a cleavage of the P–C bond and not of the C–C bond.[24]

HP=CHCH$_3$–H$_2$PCH=CH$_2$. The barrier of the HP=CHCH$_3$–H$_2$PCH=CH$_2$ interconversion is higher than the above two, at 437.5 kJ·mol^{-1}, resulting from the occurrence of a 1,3-migration. As a result of this, the geometric characteristics of the transition state (Figure 9) correspond to a hydrogen in the process of migration, partially bound to both phosphorus (P–H = 1.696 Å) and the terminal carbon (C–H = 1.55 Å), the associated overlap populations being 0.213 and 0.154. It should also be noted that this migration occurs in the σ plane with a practically flat transition state. The structure of the rest of the system is intermediate between the two isomers, i.e. a 1.403-Å C=C double bond and a P—C bond 1.733 Å long, at midway between those lengths of vinylphosphine of 1.83 Å and phosphaalkene of 1.647 Å (Figures 4 and 9).

Conclusion

The data in this work have led to the definition of the essential characters of the mechanisms of addition and insertion of singlet phosphinidene on an olefin. The addition reaction occurs according to a highly symmetric least-motion path and with no activation energy. The insertion envisioned at the σ level corresponds to a concerted mechanism with passage through a three-center transition state and an activation barrier of 25.1 kJ·mol^{-1} after CI.

The energy values obtained for phosphirane, vinylphosphine, and phosphaalkenes monomethylated on carbon and methylated on phosphorus show that the last is the most stable isomer and that vinylphosphine is the least favored, even though the four values are similar. The analysis of the electronic and structural characteristics of the four systems and the determination of the transition states associated with the main interconversions have contributed data on the mechanisms that might occur during ring-opening 1,2- and 1,3-migration.

Acknowledgment. We thank the "Centre de Calcul Vectoriel pour la Recherche for generous allotments of computer time.

Registry No. PH, 13967-14-1; C$_2$H$_4$, 74-85-1; H$_2$PCH=CH$_2$, 58436-39-8; HP=CHCH$_3$, 107257-40-9; CH$_3$P=CH$_2$, 89149-01-9; phosphirane, 6569-82-0.

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Molybdenum Cluster Chalcogenides Mo$_6$X$_8$: Intercalation of Lithium via Electron/Ion Transfer

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Received October 2, 1986

The electrochemical intercalation of lithium at 300 K into the rhombohedral molybdenum cluster chalcogenides Mo$_6$X$_8$ (X = S, Se) under formation of ternary phases Li$_x$Mo$_6$X$_8$ has been investigated with respect to the changes of composition, structure, and bonding. Complete ^{7}Li NMR phase diagrams have been established, and thermodynamic data are given. Diffusion coefficients and NMR dipolar line width demonstrate a rather high lithium ionic mobility; the reactions are fully reversible. Results are closely similar for the sulfide and selenide system. Four distinct rhombohedral phases with x = 1, 3, 3.8, and 4 could be identified. The transition from x = 1 to x = 3 is correlated with a significant increase in unit cell volume and an unusually strong decrease in NMR line shift. The latter has been interpreted in terms of a partial charge transfer with formation of triangular (Li$_3$)$^{2+}$ clusters, i.e. (Li$_3$)$^{2+}$[Mo$_6$S$_8$]$^{2-}$. For Li$_4$Mo$_6$S$_8$ the NMR shift changes again abruptly in the inverse sense to values indicating "normal" Li$^+$ ions. This is attributed to the loss in symmetry of the lithium clusters as well as the tendency for quantitative saturation of the Mo$_6$ clusters with 24 electrons (metal/semiconductor transition).

Introduction

Binary and ternary molybdenum cluster chalcogenides (Chevrel phases) with the composition Mo$_6$X$_8$ and A$_x$Mo$_6$X$_8$ (X = S, Se, Te; A = main-group or transition metal) exhibit unusual structural and physical properties and have been investigated intensively after it became apparent that many of these phases are superconducting materials with high critical temperatures and high critical magnetic fields.[1,2] The structure of the binary phases can be described by a three-dimensional arrangement of Mo$_6$X$_8$ units, which them-

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(1) Yvon, K. In *Current Topics in Materials Science*; Kaldis, E., Ed.; North Holland: Amsterdam, 1979, Vol. II, p 53.
(2) Fischer, Ø, Maple, M. B., Eds.; *Superconductivity in Ternary Compounds*; Springer Verlag: Berlin, West Germany, and Boston, MA, 1982, Vols. I and II.

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