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An Ab Initio Potential Surface for Phosphorane Fragmentation, $PR_5 \rightleftarrows PR_3 + R_2$

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Abstract: Calculations were performed to determine the favored mode of fragmentation for the $PH_5 \rightleftarrows PH_3 + H_2$ reaction using an 4-31G basis set. The addition of d orbitals to the basis set was found not to qualitatively affect the conclusions. The path of lowest energy for the reaction was found to involve a non-least-motion departure of an axial and an equatorial ligand. At the calculated transition state the axial bond was about 137% of its length in optimized PH_5 while the equatorial bond is actually slightly shorter (99% of its value in PH_5). Bonding interactions in the non-least-motion transition state are discussed as well as the relationship of the present work to other reaction types including oxidative addition. Eight degrees of freedom were investigated in constructing the potential surface.

The fragmentation of phosphoranes, $PX_5 \rightleftarrows PX_3 + X_2$, is a well-known and long-studied reaction.[1] It is possible to conceive, a priori, of different unimolecular mechanistic pathways for the process.[2] Using the trigonal bipyramid as our reference geometry, the X_2 atoms might, for instance, both originate from the axial positions of the PX_5. Alternatively, both might originate from equatorial positions, and last, one from an equatorial and the other from an axial site. We should consider also the use of a square pyramid, frequently considered as a transition state (vide infra) for ligand scrambling, as our reference geometry.

A complicating factor is that polytopal rearrangement of phorphoranes occurs with low-energy barriers.[3-5] Several different scrambling processes have been considered in the literature.[6] The problem caused by these rearrangements is simply that they provide a low-energy pathway (much lower than the calculated energy barrier for the fragmentation) for the interconversion of axial and equatorial sites in PX_5. Consequently, we need be quite careful in stating what we mean by the different reaction pathways since our starting system is fluxional.

The reaction may, of course, be viewed as occurring either forwards or backwards. An alternative perspective on the problem is obtained by considering the reverse reaction: the addition reaction of PX_3 and X_2. Here we have the PX_3 molecule bearing its lone pair interacting with a simple covalent molecule possessing both a filled σ and vacant σ^* orbitals. The lone pair is consumed during the course of the reaction and two new σ bonds are produced.

There are many reactions available for comparison having similarities in structural changes and, perhaps, in electronic effects as well. For example, the insertion reactions of singlet carbenes into the C–H bonds of saturated hydrocarbons bears a formal similarity.[7-9] While the mechanism of this reaction has been debated, most studies indicate a concerted transition state[8-10] rather than an abstraction recombination.[11] A theoretical study[10] by Dobson, Hayes, and Hoffmann favored a non-least-motion pathway.

The phosphorane addition reaction is also analogous to the oxidative-addition reactions encountered in the chemistry of coordinatively unsaturated transition metal complexes,[12-19] eq 1.

$$L_4M + XY \rightleftarrows L_4M(X)(Y) \qquad (1)$$

There have, in fact, been several studies where XY has been the hydrogen molecule. Vaska[20-22] has studied H_2 addition to $IrCl(CO)((C_6H_5)_3P)_2$. The dissociation of niobium trihydride complexes, eq 2, has been discussed.[23,24]

$$NbH_3(C_5H_5) \rightleftarrows NbH(C_5H_5)_2 + H_2 \qquad (2)$$

Iron pentacarbonyl can function as a hydrogenation catalyst.[25] The mechanism probably involves oxidative addition of H_2 to $Fe(CO)_4$, eq 3.[26]

$$Fe(CO)_5 \underset{CO}{\overset{-CO}{\rightleftarrows}} Fe(CO)_4 \underset{-H_2}{\overset{H_2}{\rightleftarrows}} Fe(H)_2(CO)_4 \qquad (3)$$

We wish to report ab initio calculations of the potential surfaces for the model system $PH_5 \rightleftarrows PH_3 + H_2$. Many other investigations[2,27-30] have been performed using PH_5 as a model. For the most part, the modelling has been fairly successful in reproducing the important aspects of the experimentally observable phosphoranes.

We wish to note several other relevant studies that have been performed. Clementi[31] studied the complex formed between NH_3 and HCl. Ohkubo, Kanaeda, and Tsuchihasi[32] have examined the least-motion approach of RX to $Co(CN)_5^{3-}$. Lucchese and Schaefer[33] have studied the charge transfer complexes formed between NH_3 or $N(CH_3)_3$ and F_2, Cl_2, or ClF. Last, we have studied the $PH_3 + H \rightleftarrows PH_4$ reaction.[34]

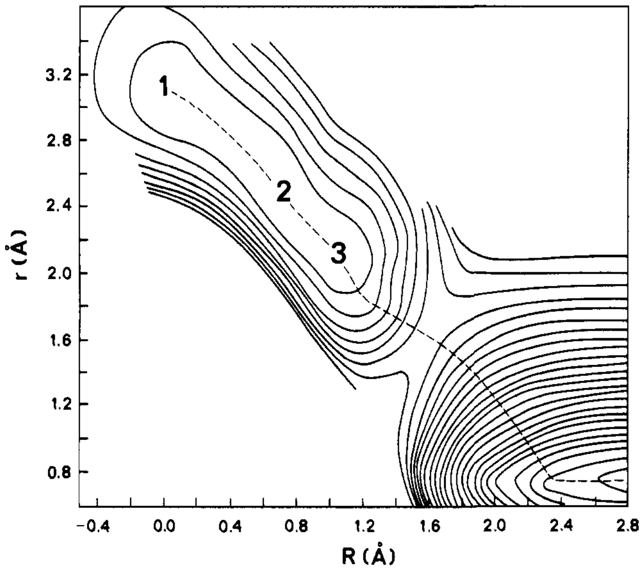


Figure 1. Ab initio (4-31G) without d potential surface for the fragmentation of PH_5 (valley at upper left) into PH_3 and H_2 (valley at lower right). The variables *R* and *r* are defined in **4**. The optimized PH_5 occurs for three different choices of *R* and *r* indicated by **1**, **2**, and **3**. The contours are at 5-kcal/mol intervals relative to PH_5. The transition state is at 32 kcal/mol and the separated PH_3 and H_2 is at −80 kcal/mol.

Calculations

The full potential surface for the PH_5 system includes 12 degrees of freedom. For ease of calculation as well as interpretation this was reduced to eight by introducing some mild constraints. A mirror plane was assumed to be present which reflected two hydrogen atoms, say H2 and H3, into each other. Furthermore H1 was assumed to lie on the mirror plane. H4 and H5, which eventually unite to form the H_2 molecule, either lie on the mirror plane or, with further reduction in the degrees of freedom, lie off of it and are also related by the reflection operation.

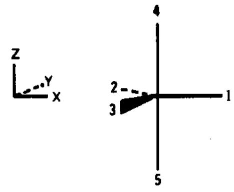
Two degrees of freedom, *R* and *r* (see below), were explicitly varied, usually in 0.2 Å increments so as to construct a two-dimensional cut through the potential surface. For each choice of *R* and *r* the remaining geometric variables (usually six) were optimized with the aid of a parabolic fitting routine.

Most of the calculations were performed using the Gaussian-70 computer[35] program utilizing an 4-31G basis set.[36] This basis set includes independent inner and outer functions for the valence shell orbitals. This allows for some flexibility in the electronic distribution as the bond lengths are stretched. The effect of d orbitals was examined through the addition of a single set of five d-type Gaussian functions with exponent 0.36 to the 4-31G sets (using the POLYATOM system of programs[37]) for various choices of *R* and *r* where the values of the other geometric variables were taken from the corresponding (s,p) optimized calculation. Calculations where noninteger nuclear charges were employed were carried out using the IBMOL-5 computer program.[38]

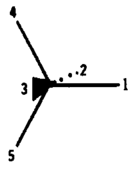
Results and Discussion

We are interested in the details of the fragmentation process: where the atoms of the H_2 molecule originate, the concertedness of the reaction, etc. As mentioned above, ligand scrambling processes serve only to complicate the problem. Various scrambling pathways have been considered. The process which has been found to have the lowest energy transition state in theoretical studies[2,27] is the Berry pseudorotation (BPR).[6a] In the BPR the bond angle between the pair of axial ligands is reduced from its original value of 180 to 120°. The reverse change occurs for a pair of equatorial ligands where the included bond angle opens up from 120 to 180°. The net result is the interconversion of an axial pair and an equatorial pair, $(H_a,H_a) \rightleftarrows (H_e,H_e)$. In our (s,p) basis set calculation the C_{4v} BPR transition state is only 1.8 kcal/mol above the D_{3h} optimized PH_5 geometry.

Structures **1–3** represent labeled PH_5 molecules which are interconverted by BPR.



1



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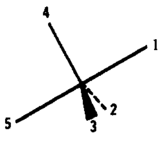
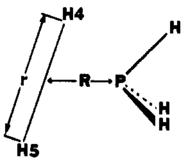


3

In passing from **1** to **2** the site exchange is $(4,5) \rightleftarrows (2,3)$. The BPR taking **2** into **3** accomplishes the interchanges $(2,3) \rightleftarrows (1,5)$. Note that the *xz* plane is a reflection plane for **1**, **2**, and **3** and furthermore that it is maintained as a reflection plane throughout the course of the BPR's used for the interconversions. Taking H4 and H5 as the departing hydrogens then **1** is the starting point for the axial, axial or (a,a) departure while **2** begins the (e,e) pathway and **3** starts the (a,e).

We now introduce the two geometric variables, *R* and *r*, used to construct the cut through the potential surface. As defined in **4**, *R* is the distance between the phosphorus atom



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and the midpoint of the line connecting H4 and H5. The distance between H4 and H5 is *r*. The *R* and *r* variables are employed to follow both the fragmentation reaction and the BPR used in the **1** → **2** → **3** interconversion.

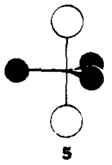
Strictly from geometry considerations and the optimized structure of PH_5 (vide infra), we may obtain values of *R* and *r* for structures **1–3**. For structure **1** we simply obtain $R = 0.0$ and $r = 3.11$ Å. For **2**, $R = 0.72$ and $r = 2.48$ Å while **3** has $R = 1.06$ and $r = 2.11$ Å. These three sets of *R* and *r* coordinates possess the same energy on our two-dimensional (*R* vs. *r*) potential surface where, as described above, the remaining geometric variables are optimized. The optimized PH_5 structure (D_{3h} symmetry with an energy of −343.025 24 hartrees, (s,p) basis set), has a PH axial bond length of 1.554 Å and an equatorial bond length of 1.433 Å. For the products we calculate an optimized PH_3 structure (at −342.025 69 hartrees) with P-H being 1.433 Å and ∠H-P-H equal to 95.1°. The H_2 molecule (−1.126 83 hartrees) has a bond length of 0.730 Å. These figures put the fragmentation products 79.9 kcal/mol lower in energy than PH_5 (1 hartree = 627.71 kcal/mol). Keil and Kutzelnigg[30] report a calculation using d orbitals where $PH_3 + H_2$ is more stable than PH_5 by 38. kcal/mol. The effect of d orbitals is the same as in our calculations, stabilizing the fragmentation products more than the phosphorane. See below for a lengthier discussion.

The first question which we attempt to answer is whether or not the (a,a), (e,e), and (a,e) modes represent distinct channels for fragmentation reaction. For example there is a 1.8 kcal/mol barrier to the interconversion of structures **2** and **3**. If we start with **2** and increase *R* do we necessarily pass to **3** (which has a larger value for *R*) or is there some other low-energy motion available to **2** eventually leading to the fragmentation products. Furthermore, we must ask if this proposed motion is separated by a barrier from the fragmentation pathway originating with **3.**

We have constructed the potential energy map of Figure 1 where we have used R and r as independent variables. The relative energy contours are at 5-kcal/mol intervals. We have used optimized D_{3h} PH_5 as the zero point in energy. The fragmentation products, $PH_3 + H_2$, lie in the deep valley at the lower right. Since the barrier to a BPR is only 1.8 kcal/mol PH_5 structures **1, 2,** and **3** lie within the same +5-kcal/mol contour. The upper left hand portion for large r and small R values has been presented before in finer detail for studies of the BPR process itself.[2,27] The first conclusion, not at all unexpected, that we may draw is that there does not appear to be any valley originating at **1** which is separated by a barrier and skirts around structure **2** on the map. It thus appears that the (a,a) mode is indistinguishable from the (e,e) mode since the former includes the latter; i.e., **2** is a way point on the (a,a) fragmentation of **1.**

If the path of least resistance is followed to still larger values of R an additional pseudorotation brings us to **3** and eventually to the fragmentation transition state having an energy approximately 32 kcal/mol above PH_5. Apparently, with five identical hydrogen substituents the departing hydrogens come, most immediately, from the axial and equatorial sites. An alternative statement is that the low-energy pathway to products starts at structure **3** and not **1** or **2.**

In an earlier paper[2] an argument, based on the nodal structure of the orbitals, was offered suggesting that the least motion (a,e) mode should be disfavored. The basic idea follows. Of the five valence shell orbitals the lowest four have nodal structures that might be smoothly transformed into the orbitals of PH_3. Thus we may examine the nodal structure of the highest occupied orbital of PH_5, **5,** to see if it may be easily converted into the σ molecular orbital of H_2, thus providing a low-energy fragmentation. However, in **5** the axial-equatorial interaction is strongly antibonding while in the σ molecular orbital of the H_2 molecule it must be bonding. The orbital reorganization would be energetically expensive and the least-motion (a,e) pathway is "forbidden". By way of contrast both the (a,a) and (e,e) pathways are symmetry allowed as may be seen by the construction of correlation diagrams.[2]



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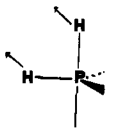
We have verified by calculations that the least-motion (a,e) pathway involves a highly energetic transition state. A portion of the potential surface was calculated where we moved the H-H moiety away from the PH_3 fragment in a simple concerted fashion. See **6.** The H-H distance and the P-H distances (but not the angles) of the PH_3 fragment were optimized. The energy barrier for this process was in excess of 50 kcal/mol.[39] This barrier might be lowered somewhat if configuration interaction calculations were performed.



6

We believe that the highly energetic concerted process described above is avoided through a non-least-motion departure. Geometries are shown in Figure 2 for approximately equally spaced points along the reaction pathway indicated by a dashed line in Figure 1. We start on the upper left of Figure 2 with PH_3 and H_2 and follow the reaction as addition takes place. As R is decreased and PH_3 and H_2 are brought together, the H-H distance, r, smoothly opens up. Judging from both the internuclear distances and the overlap populations (vide infra) bonding interactions are established with one incoming hydrogen (the equatorial one) before the other. After the new equatorial P-H4 bond has been formed H5 moves closer to the phosphorus yielding the new axial bond.

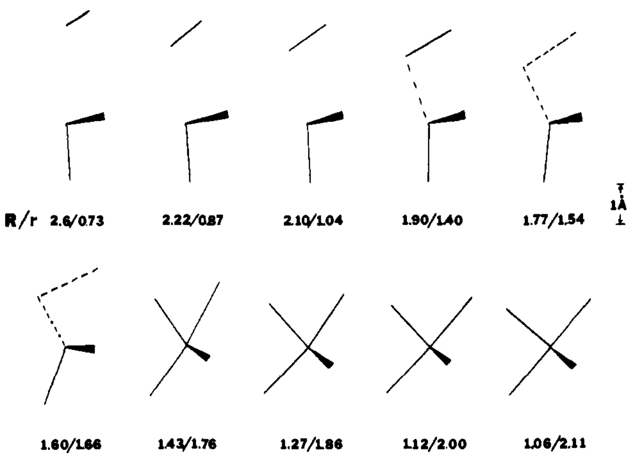


Figure 2. Geometries corresponding to approximately equally spaced points on the pathway indicated in Figure 1. The coordinates R and r refer to the variables used in constructing the potential surface of Figure 1 and are defined in **4.**

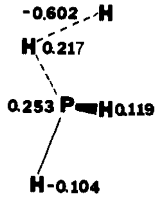
At the transition state, R = 1.60 and r = 1.66, the "axial" P-H5 bond is 2.12 Å, compared to 1.55 Å in PH_5, while the "equatorial" P-H4 bond is actually shortened a bit relative to PH_5, 1.42 vs. 1.43 Å.

The nonconcerted nature of the transition state is also reflected in the P-H overlap populations: P···H5 = −0.02, P···H4 = 0.63, while the H4-H5 overlap population is 0.09. These figures may be compared with the values for optimized PH_5 of 0.502 for axial P-H5 and 0.628 for the equatorial P-H4. Due to the sometimes erratic overlap populations produced with the 4-31G basis set we performed a calculation on the transition state using an STO-3G basis set. The same basic results were obtained: P-H5 was antibonding with an overlap population of −0.01 while P-H4 was strongly bonding at 0.59. H5 was negative, −0.59, and H4 positive, 0.11.

We note here that several tests have been performed to verify that the mirror plane of symmetry is present in the transition state. The optimization process was started for assymmetric geometries with R = 1.60 and r = 1.66 (their transition state values). As optimization of the other variables proceeded the symmetric transition state with a mirror plane was recaptured.

In molecular orbital calculations of phosphoranes[2,27-29] equatorial bonds generally appear to be stronger than the axial. This may provide a rationalization as to why the P-H equatorial bond is initially formed rather than the axial bond.

Additional insight is gained by examining the charge distribution within the transition state, **7.** The most striking fea-



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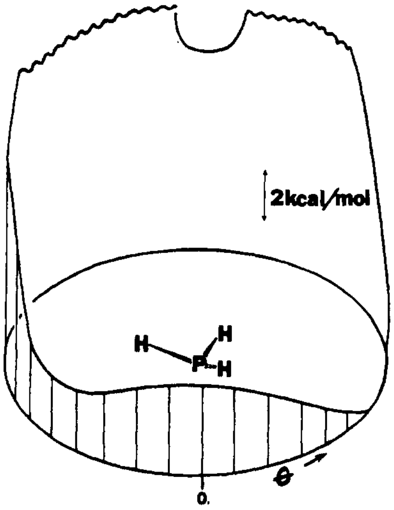


Figure 3. Schematic representation of the energy dependence of different angles, θ, of approach of H_2 to PH_3 on a disk bisecting an H-P-H angle. The distance R (see **4**) was held at 2.6 Å. The lone pair of the PH_3 lies approximately along the $\theta = 0$ ray. The energy for different values of θ is indicated by the vertical distance from the disk to the energy curve, which has three local minima. A mirror plane was maintained in the optimization process at each choice of θ.

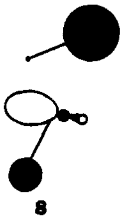
ture is the large charge separation that has been induced in the H4-H5 moiety. This charge separation of 0.804 e is in the same direction but greater in magnitude than that calculated for the PH_5 phosphorane. For our optimized D_{3h} structure the axial sites are −0.203 while the equatorials are +0.031, for a charge separation of 0.234 e.

On the basis of charge distribution and bonding the transition state would seem to much more resemble that for a nucleophilic displacement reaction than that for a concerted addition.

The charge distribution in the "H_2" portion of the transition state suggests that an atom of high electronegativity, for instance the F in ClF, would prefer to enter directly into the axial site rather than first enter an equatorial position and then reach an axial site via rearrangement. We have tested this argument by varying the nuclear charges on the "H_2" fragment in the transition state. When H5 has a nuclear-nuclear charge of 1.05 and H4 was 0.95 the energy was −342.995 09 hartrees. If the nuclear charges were interchanged making H4 more electronegative an energy of −342.962 27 hartrees was obtained. The energy difference, 20.6 kcal/mol, is large and clearly favors direct entry of the more electronegative atom into the axial site.[40]

In addition to the charge distribution of the transition state just discussed there is another reason why the less electronegative atom of the "H_2" should form the first bond. There is donation of electron density from the phosphine lone pair into the "H_2" σ^* orbital (vide infra). When H5 is more electronegative than H4 the σ orbital will be predominantly on H5 and the σ^* on H4. This minimizes the repulsive interaction of the σ orbital and the lone pair and, simultaneously, facilitates the (lone pair) → σ^* donation.

In providing a rationale for the nature of the transition state we need to examine the highest occupied molecular orbital of the transition state, **8**.



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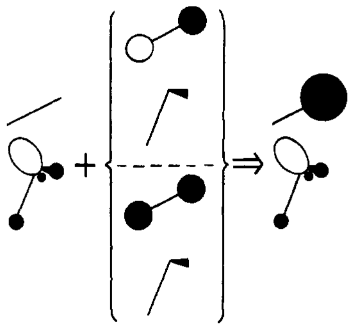
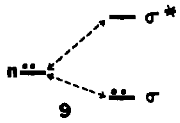
Scheme I



Within the orbital **8** there is large buildup at H5 explaining the charge distribution of **7**. We may easily understand its makeup. **9** shows the interaction of the phosphine lone pair (n) with the lower lying σ and higher σ^* orbital of H_2.



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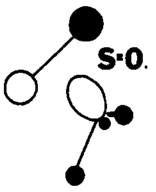
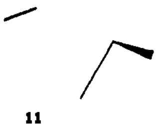
Following the rules of perturbation theory,[41] the σ^* is mixed-in in a bonding fashion, since it is higher in energy than the lone pair whereas the lower lying σ is mixed-in antibonding. The result is a cancelation of contributions occurring at H4 and a buildup at H5. This is shown schematically in Scheme I. The mixing in of the σ^* orbital is stabilizing, tending to decrease the energy of the transition state. The geometric requirement for the σ^*-lone pair interaction is that of a non-least-motion approach. This follows since the overlap, S, of σ^* and the lone pair is nearly zero in the least-motion geometry[42] of **10**.



10

We have further investigated the geometries of approach for PH_3 and H_2 in a slightly different way. This was done by holding R fixed and varying the angle of approach between the two molecules. θ is defined as the angle between the local C_{3v} axis of the PH_3 and the vector R. (The PH_3 lone pair lies at $\theta \approx 0$.) In this study the other geometric variables, including r, were optimized. The resulting E vs. θ curve, for R held at 2.6 Å, is displayed in Figure 3. Three minima are apparent. The lowest occurring at $\theta \approx 68°$ lies on the reaction pathway of Figure 1 and is depicted in the upper left corner of Figure 2. The next higher (by 2.2 kcal/mol) minimim occurs at $\theta = 313°$ and is shown in structure **11**. These two minima for systems with mirror plane symmetry are in fact connected by rotational motion of the H_2 and PH_3 with respect to each other. This rotational motion, involving geometries not having a mirror plane, obviates the need to traverse the energy barrier of $\theta = 0$ when going from one minimum to the other.



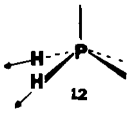
11

The structure shown in **11** is similar to that shown in Figure 2 in that one of the H_2 atoms is decidedly closer to the phosphorus than the other. The manner of approach, shown in **11**, would be expected to be of higher energy than that of Figure

2 since formation of the second P-H bond would be difficult. When R is decreased to 2.0 Å the two minima still persist but now the energy difference has increased to about 12 kcal/mol.

The geometries assumed along our reaction pathway and depicted in Figure 2 depend on the choice of potential surface variables. For instance had we chosen R to measure the distance to H4, say, and not to the midpoint of H4-H5 then our surface in Figure 1 would be different and so would the geometries of Figure 2 but the qualitative conclusions concerning the nature of the transition state would be the same. In this context we draw attention to the work of Lucchese and Schaefer[33] who found that the preferred geometry of charge transfer complexes $NR_3 \cdot XX'$ ($R = H, CH_3$ and $X,X' = F,Cl$) is C_{3v} with the XX′ molecule approaching along the C_{3v} axis of the NR_3 molecule.

We also investigated the possibility that the departing atoms might be best described as originating from one side of the square in the C_{4v} BPR transition state, **11.** The plane of the page is maintained as a symmetry plane. The pathway is symmetry forbidden as may be seen by constructing a correlation diagram. A slice through the potential surface was roughly constructed where, as in **12,** two pairs of hydrogens were kept as mirror images of each other. Again R and r were the coordinates investigated. The energy barrier was calculated to be in excess of 60 kcal/mol. Due to the limitations of a single configuration calculation the problem was not examined in detail.



12

Other pathways originating with the square-pyramid structure are included in the detailed study of Figure 1. The square pyramid occurring between **1** and **2** serves as the starting point for the basal-basal (diagonally related) departure while the square pyramid occurring between **2** and **3** is the starting point for the apical-basal pathway.

We investigated the effects of d-orbitals by performing a number of additional calculations with a set of d orbitals on our two-dimensional slice through the potential surface. For each choice of R and r examined we utilized the (s,p) optimized geometries. The resulting "with d" potential surface was lower in absolute energy than the one without d presented in Figure 1. The overall qualitative features were the same but unfortunately the two surfaces were not separated by a constant energy difference. The (no d-d) energy difference ranged between 36 (in the $PH_3 + H_2$ region) and 63 kcal/mol (in the PH_5 region).

The present study may be germane to the detailed mechanism of the oxidative addition mechanism undergone by unsaturated transition metal carbonyls. Elian and Hoffmann[43] have examined the orbitals of transition metal carbonyl fragments, $M(CO)_{n-1}$, obtained by dissociation, eq 4.

$$M(CO)_n \rightleftarrows M(CO)_{n-1} + CO \qquad (4)$$

We wish to consider the interaction of an incoming H_2 with different types of metal donor orbitals. If the dominant interaction is donation from an orbital similar to **13** then the reaction pathway would be similar to that just described for $PH_3 + H_2$. On the other hand, if the metal donor orbital more closely resembles **14** then a concerted reaction might be expected with both M-H bonds forming simultaneously, through donation into the H_2 σ^* orbital, **15.** We refer the reader the Elian-Hoffmann paper[43] for discussions as to orbital occupancies and orderings in different geometries with various ligands.

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14

15

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References and Notes

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Stability and Reactivity of the Si–C Double Bond

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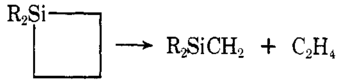
Abstract: Properties of the Si=C group are investigated by means of quantum mechanical ab initio computations of the lowest singlet and triplet states of $SiCH_4$ and the cycloaddition of $SiCH_4$ to 1,3-disilacyclobutane, $Si_2C_2H_8$. Extended basis sets are employed and effects of electron correlation are included. The pertinent results are (1) $SiCH_4$ has a planar π-bonded singlet ground state about 28 kcal/mol below the lowest triplet which has perpendicular structure; (2) the bond strength of the Si-C 2pπ-3pπ bond as determined by the rotational barrier is ~46 kcal/mol; (3) the barrier for the cycloaddition is less than 14 kcal/mol and the reaction energy ~−76 kcal/mol, indicating great reactivity of the Si=C group which results from the considerable bond polarity.

I. Introduction

One of the most striking features of silicon chemistry is the complete absence of compounds with multiple bonds of pπ-pπ type that are stable under the usual conditions. However, the existence of short-lived intermediates of the form $R_2SiCR'_2$ has been concluded, e.g., from the pyrolysis of silaolefins;[1-5] an almost up-to-date review of this and related problems has been given by Gusel'nikov et al.[1] A typical case is the thermal decomposition of monosilacyclobutanes which yields 1,3-disilacyclobutanes and ethane, where kinetic data support the following mechanism.[6,7]



(1)

(2)

Whereas the mechanism (1, 2) seems to be generally accepted, there has been much discussion and speculation concerning the electronic structure of the intermediate R_2SiCH_2. The problem here is the relative stability of the π-bonded closed shell (singlet) structure with polarized Si-C bonds

$$R_2Si^{\delta+}{=}C^{\delta-}H_2 \qquad (3)$$

vs. the open-shell triplet 1,2-diradical state

$$R_2\dot{Si}{-}\dot{C}H_2 \qquad (4)$$

From experiments one has, in our opinion, so far not been able to establish beyond doubt which of the two structures (3) or (4) is the more stable one, although preference is usually given to (3).[1-5]

It was the aim of the work described in this paper to investigate the stability of the Si-C double bond by means of quantum mechanical ab initio calculations. For this purpose we first performed elaborate computations for the molecule $SiCH_4$, which is, at least from the computational point of view, the simplest conceivable compound of this class. Generation and trapping of $SiCH_4$, which turned out to be a very reactive intermediate, has been reported by Golino[5b] et al. With these computations we first of all want to decide whether (3) or (4) is more stable—it turns out that (3) is ~28 kcal/mol lower in energy than (4)—and furthermore determine properties of $SiCH_4$ like bond polarity, π-bond strength, etc., which provide hints on the chemical behavior of this molecule.

We finally investigated the reaction

$$2SiCH_4 \rightarrow Si_2C_2H_8 \text{ (1,3-disilacyclobutane)} \qquad (5)$$

which is a model case for (2), to determine the corresponding barrier ΔE_B and reaction energy ΔE. These results then provide detailed answers to the question of the stability and reactivity of the Si-C double bond in $SiCH_4$ and also for related compounds.

After completion of the present study Strausz, Gammie, Theodorakoupoulos, Mezey, and Czismadia[8] (SGTMC) have published an ab initio investigation of the lower electronic manifold of $SiCH_4$. Our results are partly in considerable disagreement with those of SGTMC, who predict the triplet to be 1.4 kcal/mol lower in energy than the singlet. This as well as other deviations from the present results can be attributed to the rather small basis set and the methods used by SGTMC, who have neglected effects of electron correlation.

II. Method of Computation

Most results reported in the present paper (e.g., geometrical parameters for the various states of $SiCH_4$, barrier and reaction energy for reaction 5) were obtained by means of closed and open shell RHF computations, which certainly are sufficiently accurate for this purpose. However, the correlation energy—by definition neglected on the HF level—has in general a pronounced influence on the energy difference between closed shell singlet and open shell triplet states.[9] The correlation energy of the π-bonded ground state of C_2H_4 exceeds the corresponding one for the lowest triplet (vertical excitation) by ~20 kcal/mol[9] and similar relationships have