Primary Reaction of the Titanium-Catalyzed Oligomerization of Phosphorus in the Gas Phase

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Abstract: The primary reaction of titanium-catalyzed oligomerization of phosphorus using methylphosphine as a reagent has been studied with a highly accurate quantum mechanical procedure. The reaction proceeds as a two-step process with the titanium atom catalyzing the migration of a hydrogen atom from carbon to phosphorus by delocalizing electrons into its unoccupied d orbitals. Thus in the transition state of the second step it has been clearly identified a two-electron three-center bond among titanium, the phosphorus, and the migrating hydrogen atom, which drives the hydrogen from the carbon over to the phosphorus.

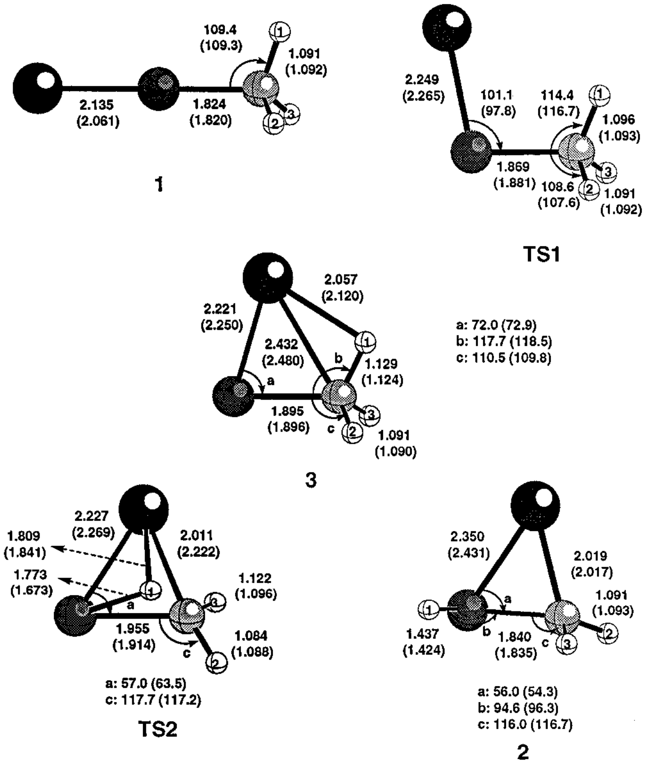

Figure 1. Geometrical parameters of the various stationary points and transition states at the B3LYP/TZVP+G(3df,2p) level of theory. Values in parentheses correspond to the geometrical parameters of the excited states. Bond lengths are reported in Å, and bond angles, in deg.

Catalytic capabilities are some of the most valuable properties of the transition metals; therefore, substantial research efforts have been devoted to unveil the mechanisms operating in their catalytic reactions.[1] Even though it is widely recognized[2,3] that a better understanding of the elementary reaction steps and the structures of possible intermediates and transition states involved in the catalytic reactions would be crucial for a better design and utilization of improved catalysts, this is still a major challenge because the details of these processes are not well understood yet.[4]

One major problem is that isolating one single property out of the various factors that take place in chemical reactions is difficult. This has triggered a renewed interest in gas-phase behavior,[5] since these studies are particularly well-suited for the elucidation of basic properties without being hampered by disturbing effects that prevail in condensed phases.

Recently, attention has been drawn to the catalytic properties of transition metals in the polymerization of phosphorus. It has been found that the titanium ion produces phosphorus oligomers when it reacts with methylphosphine in the gas phase.[6] This is an interesting reaction that provides an alternative route to the synthesis of phosphorus compounds, analogues to well-known hydrocarbons, exhibiting remarkable features such as the recently described[7] one-electron phosphorus−phosphorus bonds.

The major product of the primary reaction of Ti^+ with methylphosphine, $TiCH_3P^+$, has been the subject of recent intense investigations.[6] Particular attention has been paid to the determination of the structure of the resulting main product, $TiCH_3P^+$. Two probable structures **1** and **2** in Figure 1, have been proposed and examined by various experiments. Indeed, it has been found that Ti^+ eliminates only D_2 from CH_3PD_2, an experimental result that gives support to structure **1** in favor of **2**. However, detailed analysis by CID, H/D exchanges with D_2O and other substrates, and ion−molecule reactions of the product ion after the H/D exchange all are suggestive of structure **2**. Consequently, it has been postulated that **1** is an intermediate which rearranges to the more stable structure **2**.

In this article we present results from our high-level ab initio calculations on these species. We will show that the **1** → **2** rearrangement is a two-step process involving another intermediate structure **3** and that all three species lie close in energy.

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Table 1. Total (in au) and Relative (in kcal/mol) Energies for the Various Stationary Points Characterized

stuct	state	B3LYP+ZPVE	CCSD(T)	ΔCCSD(T)+ΔZPVE
1	^{2}E	−1230.425 41	−1229.246 30	00.00
1	$^2A_1$	−1230.408 54		
TS1	$^2A''$	−1230.411 96	−1229.229 45	10.03
TS1	$^2A'$	−1230.411 54		
3	$^2A''$	−1230.422 88	−1229.244 50	00.74
3	$^2A'$	−1230.418 84		
TS2	$^2A(d_{z^2})$	−1230.367 73	−1229.187 34	32.88
TS2	$^2A(d_{yz})$	−1230.353 61		
2	$^2A(d_{z^2})$	−1230.433 14	−1229.254 48	−7.66
2	$^2A(d_{yz})$	−1230.425 54		

[a] The ZPVE was calculated with the B3LYP method. The basis set used was the TZVP+G(3df,2p) set.

All structures of Figure 1 were optimized with the B3LYP[8,9] functional and a triple-ζ quality basis set [TZVP+G(3df,2p)[10−13] for the metal and 6-311++G(2df,pd)[14] for the C, P, and H atoms], followed by a frequency calculation at the same level of theory in order to assess whether each corresponds to a real minimum (all force constants positive) or to a transition state (all but one positive force constants) and to estimate the zero-point vibrational energy correction (ZPVE). To improve the energies, subsequent single-point calculations were carried out on these structures at the CCSD(T)/TZVP+G(3df,2p) level of theory[15−21] and then corrected with the ZPVE correction alluded to above. The 1s electrons of C and 1s to 2p electrons of the metal and the P atoms were frozen in the CCSD(T) calculations. This procedure has been tested in previous works by our group[22−24] and also worldwide.[25−30] Energies may be found in Table 1, and frequencies, in the Supporting Information section.

Our calculations show that structure **1** has C_{3v} symmetry and its ground electronic state is ^{2}E.[31] The Ti atom bears the positive unit charge, and it has a double titanium phosphorus bond and a single P−C bond. Its unpaired electron lies on the titanium's $d_{x^2-y^2}$ orbital, giving rise to the ^{2}E state. An excited $^2A_1$ state with the unpaired electron occupying the d_{z^2} orbital of titanium has also been characterized 10.58 kcal/mol higher in energy.

Since the E doubly degenerate C_{3v} irreducible representation splits into $A' + A''$ irreducible representations of the C_s point group, it is clear that insertion of Ti into the P−C bond will proceed along either A' or A'' potential energy surfaces. We have found that the $^2A''$ path is the one which lies lower in energy.

The first step involves **TS1**, in which the imaginary frequency corresponds to Ti−P−C bending, lying 10.04 kcal/mol above structure **1** on the $^2A''$ PES. Its first electronically excited state belongs to the $^2A'$ irreducible representation and lies only 0.27 kcal/mol higher in energy than the $^2A''$ ground state.

Following the Ti−P−C bending mode leads to structure **3**, which also has C_s symmetry. Its $^2A''$ ground electronic state is only 0.73 kcal/mol higher in energy than **1** according to our best energy calculation.[32] The excited $^2A'$ electronic state of **3** is 2.54 kcal/mol above the ground state. It is observed from Figure 1 that both Ti−P and P−C bond lengths have been elongated with respect to **1**. The natural bond orbital analysis of our best Kohn−Sham orbitals shows a Ti−P double bond and a P−C single bond. However, both the P−C and the $C-H_1$ bonds are found to be delocalized substantially over the vacant d orbitals of Ti. Indeed, the calculated second-order interaction energies are 18.75 and 14.84 kcal/mol for the $\sigma_{P-C} \rightarrow n_{3d_{xy}+3d_{x^2-y^2}}$(Ti) and $\sigma_{C-H_4} \rightarrow n_{4s+3d_{z^2}}$(Ti) interactions, respectively. Notice this species has attached to the carbon atom two equivalent hydrogens and a third distinct one (H_1), bound more weakly to the carbon atom.

The second step shown in Figure 2 requires overcoming an activation barrier three times higher than the first step. The ground state of **TS2** has been located 32.88 kcal/mol above **1** and 32.15 kcal/mol above the $^2A''$ ground state of **3**. When the C_s species **3** moves into C_1 symmetry, the various d orbitals of Ti can all mix and we find that the most stable configuration is different from **3**. The unpaired electron of **TS2** is on the $3d_{z^2}$ orbital of Ti. An excited state with the unpaired electron occupying the Ti $3d_{yz}$ orbital has also been characterized 8.86 kcal/mol higher in energy than the ground state of **TS2**. This transition state is associated with the H_1 migration to the phosphorus atom. It should be pointed out that, in the CID studies, loss of CH_3 only occurred at very high energies implying that a rearrangement from $TiPCH_3$ must occur at lower energies.[6] Our CCSD(T)/TZVP+G(3df,2p) level calculation predicts that the $TiPCH_3 \rightarrow TiP + CH_3$ reaction requires 58.36 kcal/mol, an energy much higher that this barrier to rearrangement.

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(31) Normally, an ^{2}E state of a molecule with C_{3v} symmetry would experience Jahn−Teller distortion. However, in this case the singly occupied orbital rests entirely on the Ti atom, an atom which is bonded to only one other. Thus, no distortion to reduce the C_{3v} symmetry occurs.

(32) Notice that single-reference methods such as both B3LYP and CCSD(T) do not represent a correct description of a degenerate state like ^{2}E, for which a multireference method is needed. Nevertheless we have carried out a calculation of the relative energy between structures **1** and **3** at the CASPT2/ano-s level of theory, with an active space of 5 electrons in 8 orbitals. Two different levels of correlation at CASPT2 level have been used. In the first, 15 core orbitals were frozen, while in the second only 11 core orbitals were frozen (correlating also the 3s and 3p orbitals of Ti). The values obtained for the difference in energy between structures **1** and **3** is at these two levels of correlation respectively 1.64 and 0.31 kcal/mol. These values are in excellent agreement with the values reported at the CCSD(T)//B3LYP (0.73 kcal/mol) and B3LYP/TZVP+G(3df,2p) (1.59 kcal/mol) levels of theory. This indicates that our CCSD(T)//B3LYP is satisfactory. See also refs 23−25, 27, 29, and 30 for further support of this point.

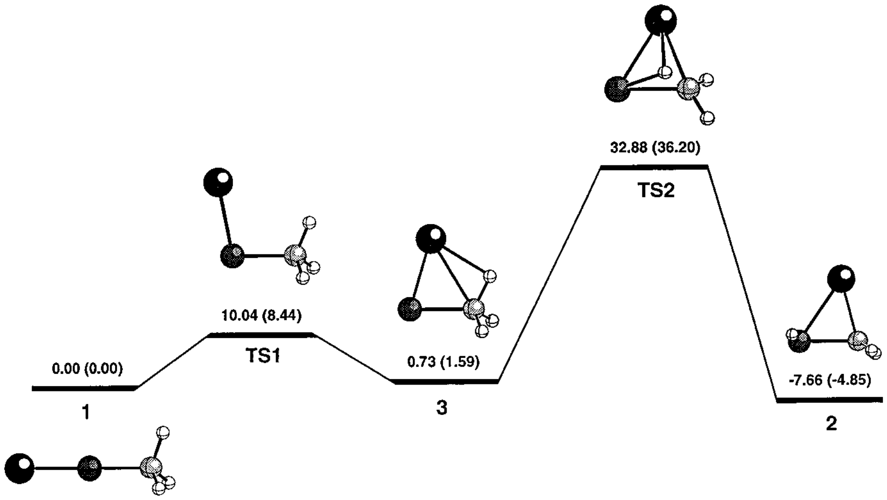

Figure 2. CCSD(T)/TZVP+G(3df,2p) potential energy surface. In parentheses are the B3LYP/TZVP+G(3df,2p) values. Energies given are in kcal/mol and are relative to structure **1**, $TiPCH_3^+$ (^2E).

The NBO analysis of **TS2** suggests that the Ti−C bond builds at this stage as we have been able to find a natural Ti−C bond orbital with a population of 1.7 electrons. It is also remarkable that we have found a Ti−H_1−P two-electron three-center natural bond orbital, indicating that the migration of H_1 from the C to P is assisted by the metal atom. Indeed at this stage we have not been able to find any C−H_1 bonding interaction.

The resulting species of this second step has the structure **2**. This three membered ring cycle molecule is more stable than **1**. According to our best energy calculation its ^2A ground electronic state lies 7.66 kcal/mol below the ground state of **1**. An ^2A excited state of **2** has also been found 4.77 kcal/mol higher with respect to the ground state of **2**. The titanium atom bears almost the whole positive charge and the unpaired electron occupies the d_{z^2} (d_{yz}) in the ground (excited) state of **2**, as was the case in **TS2**.

In conclusion, the present study demonstrates that the primary reaction of the titanium-catalyzed olygomerization of phosphorus using methyphosphine as a reagent proceeds as a two-step process. The titanium atom catalyzes the migration of a hydrogen atom from carbon to phosphorus through delocalization of electrons into the unoccupied d orbitals of Ti. We have been able to unveil the mechanism of the catalytic action of Ti by analyzing the natural bond orbitals of **TS2**, which clearly identifies the formation of a titanium−carbon bond and the existence of a two-electron three-center bond among the titanium, the phosphorus, and the migrating hydrogen atom. This metal-assisted hydrogen migration sheds light on the catalytic behavior of the metal and might be instrumental in understanding the role of transition metals in these important polymerization reactions of phosphorus.

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Supporting Information Available: A table of vibrational frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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