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Ruthenium-Catalyzed Olefin Metathesis: A Quantum Molecular Dynamics Study

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Abstract: Chemical reactions are usually performed in solvents. The course of the reaction varies with solvent, temperature, etc. Solvent molecules are usually not taken into account in quantum simulations due to the rising computational effort. However, their ability to transfer heat (kinetic energy) to and from the reacting species can be incorporated in the simulations. We demonstrate that different chemistry follows by varying absolute simulation temperature and the range for temperature fluctuations in Car−Parrinello dynamics simulations applied to ruthenium catalyzed metathesis reactions. The bisphosphine $Cl_2(PH_3)_2Ru{=}CH_2$ complex and its monophosphine equivalent were taken as model compounds for the Grubbs catalyst. Depending on temperature conditions set in the molecular dynamics simulations, the interaction of these ruthenium−phosphine catalysts with ethylene revealed insertion, the formation of a metallacyclobutane, or a pure metathesis reaction. It was found that selective bond vibrational activation is required to induce metathesis activity. A comparison with recent experimental results from Grubbs et al. (*J. Am. Chem. Soc.* **1997**, *119*, 3887) shows that the results of our simulations reveal and lend support to the mechanism proposed by Grubbs. These include, in the order of appearance in the reaction scheme, the relative easiness of Cl−Ru−Cl cis−trans configurational exchange, carbene rotation and the loss of one phosphine, formation of a metallacyclobutane intermediate, and finally completion of the metathesis reaction. The presence of a small fraction of the monophosphine complex (the reaction proposed in Scheme 1, which was adopted from Grubbs et al.) is confirmed by the present simulations. Starting from the observation that selective bond excitation is necessary to exhibit reactivity, the higher activity of the monophosphine system compared to bisphosphine complexes reported by Grubbs et al. can be understood. We stress that we have also found that the bisphosphine is active, which also agrees with the experimental data. Finally, the fact that ruthenium−carbene complexes based on sterically crowded phosphines give higher metathesis activity, can be rationalized by their intrinsically more labile Ru−P bonds as indicated by longer Ru−P bond lengths.

1. Introduction

During the past few years, first-principles molecular dynamics (MD) simulations have been successfully applied to chemical reactions catalyzed by transition metals. Since the first paper,[1] a number of groups have reported similar investigations, using either the original Car−Parrinello method[2] or the CASTEP[3] code.[4−10] Meanwhile the chemical applications of the method have been extended to, e.g., the mechanical properties of crystalline polymers.[11] Whereas in some studies no explicit use was made of the dynamical aspects of the reaction, others report well-defined, usually anticipated reaction pathways. The latter involved simulation with either a constrained-dynamics approach, or without a constraint. Furthermore, the calculations were performed either at constant temperature or microcanonically; i.e., temperature was allowed to evolve freely while starting at $T = 0$ K. In all these cases the primary intention was to study often anticipated reaction pathways, some of which had been studied independently by traditional static quantum methods (Hartree−Fock or density functional).

In real chemical reactions there is often a solvent, and the course of the reaction may vary strongly with solvent, temperature, etc. It is this aspect which we intend to study. Solvent molecules, present in most chemical systems, are usually not taken into account in quantum simulations due to the rising computational effort. However, their ability to transfer heat (kinetic energy) to and from the reacting species can be incorporated in the simulations. We will demonstrate that different chemistry may follow by varying the temperature. Varying temperature control may be interpreted as modifying the capability of exchanging kinetic energy with the environment, and therefore with the type of solvent molecules or the

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Scheme 1

density of the solvent. The use of quantum dynamics simulations to study such variations in chemistry will be demonstrated for the metathesis reaction involving a ruthenium−carbene complex interacting with ethylene.

Recently, olefin metathesis has attracted considerable attention, both for reasons of fundamental scientific interest as well in regard to potential practical applications.[12] In particular, the group of Grubbs has studied the metathesis of strained cyclic,[13,14] or low strain cyclic olefins,[15,16] exocyclic olefins,[17] straight-chain alkenes,[15] and the reactivity of triphenylphosphines versus tricyclohexylphosphines[15] as ligands. The chemistry was based on the use of a well-defined ruthenium−carbene catalyst. Details on the reaction mechanism remained unresolved. However, in a very interesting recent paper,[18] Grubbs et al. have presented experimental data including a detailed study on the catalyst $Cl_2(PCy_3)_2Ru{=}CHPh$ to investigate the mechanism of olefin metathesis using this class of ruthenium−carbene catalysts. Their results clearly indicate that the most active species is a monophosphine complex, with the bisphosphine complex being less active. The higher activity of the monophosphine was explicitly demonstrated by addition of CuCl or $CuCl_2$ to the bisphosphine complex, which are capable of binding a phosphine group captured from the ruthenium complex. The pathway considered most probable by Grubbs is illustrated in Scheme 1.

Parallel to the experimental investigation by Grubbs et al., we had started a theoretical study involving quantum simulations in order to obtain further detail on the mechanism of the ruthenium-based olefin metathesis. Phosphines in general may lead to metathesis reactions, but donating phosphines do a particularly good job in this respect. The steric and electronic effects of the ligands may be expressed in Tolman factors.[19] The steric factors for PH_3 and PCy_3 are $\theta = 87°$ and $\theta = 170°$, respectively, whereas the electronic factor χ has the numerical value 8.3 and 0.1 for these two ligand types. For computational purposes, however, we have limited ourselves to the PH_3 ligand in the present study. We will address the stability of the bisphosphine complex $Cl_2(PH_3)_2Ru{=}CH_2$ (**1**). Grubbs et al. have argued that the monophosphine complex is particularly active, but present for less than 5% (as measured from the amount of unbound phosphine). We studied this question by a straightforward dynamics simulation of the complex in vacuo. If a bond is unstable, simulation of that species in vacuo generally reveals bond breaking at the subpicosecond time scale, i.e., at the time scale of the slowest motion in that system, as was previously shown for alkyl bridged dialuminum complexes.[20] A second issue which we will address is the chemistry that follows when adding an ethylene to the ruthenium−carbene complex; i.e., we will study the $Cl_2(PH_3)_2Ru{=}CH_2/C_2H_4$ bisphosphine complex (**2**) and the monophosphine complex $Cl_2PH_3Ru{=}CH_2/C_2H_4$ (**3**). When the conclusions put forward by Grubbs et al. are correct, at least one Ru−phosphine bond is somewhat labile. Following that concept, we have studied which chemical reactions may be induced by putting various quantities of energy into the labile Ru−P bond.

2. Molecular Dynamics Strategy

While molecular dynamics simulations may be performed at a fixed temperature, in a real-world system there is a Maxwell−Boltzmann distribution of velocities, and thus a distribution of kinetic energies. Although temperature is a macroscopic quantity, in molecular dynamics simulations a temperature is calculated from the atomic velocities, i.e., the kinetic energy, of the limited set of atoms present in the periodic cell. With reference to a true many particle ensemble, particles which are in the high-end tail of the Maxwell−Boltzmann velocity distribution should be described with a high “temperature” in the simulation. It follows from the Maxwell−Boltzmann distribution of velocities for a given temperature T that a nonnegligible number of molecules has a kinetic energy which is four to nine times higher than the average value.[21,22] According to the equipartition principle, each degree of freedom contributes $^1/_2kT$ to the total energy of a system, and, therefore, individual molecules in the high-end tail of the Maxwell−Boltzmann velocity distribution may have energies in some degrees of freedom as high as $2-4kT$. For $T = T_{room}$ this implies a kinetic energy of the order of 1−3 kcal/mol. For this reason energetic barriers of that magnitude can be easily overcome by the kinetic energy present in a substantial fraction of the molecules of the ensemble, and calculated barriers of a few kcal/mol are therefore relatively insignificant with respect to the reaction rate, providing the collisions take place in the right geometry. Moreover, simulation temperatures several times higher than ambient temperature are still realistic with respect to a subset of the molecular species with higher than average molecular speeds. This is one type of approach applied in the present work.

When a true energetic barrier is present, i.e., the rate is not diffusion limited, this barrier can be overcome in the real experimental system when there is sufficient vibrational energy in the reaction coordinate. In static quantum mechanical calculations the energy barrier tends to be investigated by stepwise going along the reaction path, involving constraint geometry optimization, and subsequently deriving the barrier

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height from the potential energy versus reaction coordinate plot. In a molecular dynamics simulation, the analogue is to perform a constrained dynamics simulation. This method has the advantage that one may obtain, quite directly, the free-energy barrier ΔG, while retaining dynamical aspects of the reaction.[7] However, for practical simulations the masses of the nuclei were increased in the work in ref 7, while the reaction path is enforced by the constraint.

Another, thus far unexplored, alternative is to concentrate a surplus of potential energy in a certain bond at the beginning of the simulation. This is a realistic situation in a real experimental system as species will react when (i) they have sufficient energy to overcome an energetic barrier (i.e., these molecules are usually to be found in the high-end tail of the Maxwell−Boltzmann velocity distribution), and (ii) the internal kinetic energy in the molecule should preferably be concentrated in bonds that may form the reaction coordinate or which are directly related to that coordinate. Thus those molecules will react which have sufficient kinetic energy concentrated in the right bonds. Simulations were subsequently performed with energy concentrated in the Ru−P bond(s). The technical procedure is briefly described below.

In the program we have employed to perform the simulations, the only practical way to deliberately put excess kinetic energy in a bond was to start from a compressed bond length. This does not provide a good tool to set the initial kinetic energy, or temperature, for the simulation. Therefore, starting from a compressed bond, subsequent rescaling of the atomic velocities during the first femtoseconds of the simulation enables us to control the initial excess kinetic energy by setting a limit to the temperature. A larger allowed temperature window leaves more excess kinetic energy in the, originally compressed, bond. In that way we obtained selective bond activation.

After the initial phase in the simulations in which the temperature window is used to set the initial excess kinetic energy in specific bonds (<30 fs), in the major part of the simulation the temperature window has a relation with the environment in a real, experimental system. When the single molecule “temperature” strongly deviates from that of the environment, the transfer of kinetic energy to the environment increases. This leads to adaptation of the molecule’s kinetic energy to the environment, which in the simulation is accomplished by rescaling the atomic velocities. However, in most of the simulations reported here, in particular the simulations performed at $T = 400 \pm 250$ K and $T = 400 \pm 500$ K, the simulation temperature did not exceed its set limits after the named initial phase of the simulation. The initially set larger window then mimics a slower exchange of kinetic energy with the environment, as withdrawing of adding kinetic energy to the system by rescaling the atomic velocities represents the effect of a real solvent (this is also known in classical molecular dynamics as an external heat bath).

Finally, during the dynamics simulation, the potential energy will be transferred into kinetic energy. Because we do not impose a reaction path, the system still has a certain freedom to choose its own. In this way it is possible to gain explicit information on dynamical aspects of the reaction and on *alternative* reaction pathways within acceptable computing times and without the necessity to increase the masses of the nuclei.

3. Computational Details

For a description of the soft- and hardware employed, and for aspects of the simulations, we refer to refs 1 and 10. With respect to the present simulations on the ruthenium-based metathesis reaction, the largest molecular complexes treated had a maximum dimension of 7−8 Å, and were placed in a cubic box of length 11.6 Å. There is thus some vacuum around the reacting complex, and we are effectively studying a reaction in a vacuum as is common in traditional quantum calculations of the Hartree−Fock and the density functional type. A Vanderbilt type pseudopotential was used for ruthenium, and its valence electrons treated explicitly were $4s^2 4p^6 4d^7 5s^1$. An energy cutoff of 25 Ry was employed for the plane-wave expansion. Gradient corrections according to Perdew[23] and Becke[24] were included. Before starting a molecular dynamics simulation, the molecular structure was energy minimized using a steepest descent routine.

One type of simulation we performed is a microcanonical simulation in which the total energy of the system is kept constant. During the dynamics simulations the molecular structures fluctuate (i.e., the atomic positions move) accompanied by changes in the potential energy. Because the total energy is constant, changes in the potential energy are reflected in corresponding changes in the kinetic energy, and therefore in temperature. A second type of simulation was performed in which the temperature was maintained at a given temperature by rescaling the atomic velocities. This resetting of the temperature was done when the temperature was deviating more than a given offset from the average. This type of simulation is therefore characterized by a temperature $T \pm \Delta T$, e.g., $T = 400 \pm 250$ K.

4. Results and Discussion

4.1. Simulations Starting from Equilibrium Ru−P Bond Lengths. a. Energy Minimization. We first studied the bisphosphine complex (**2**) with ethylene in order to investigate any barrierless reactivity. The geometry of the ruthenium bisphosphine complex (**1**) after optimization may be compared to experimental geometries obtained on crystals. Calculated bond lengths compare favorably with the X-ray data on similar complexes, presented by Nguyen et al.[13,15] A calculated Ru−P of 2.34 Å is to be compared to an experimental value of 2.39 Å, and a calculated Ru−C distance of 1.90 Å versus an experimental value of 1.89 Å. The calculated Ru−Cl distance of 2.35 Å compares favorably to the experimental value of 2.34 Å. Bond angles initially seem to agree much less well. The P−Ru−P angle for the energy minimized structure is close to 180°, whereas the experimental value in the crystal is 167°. However, the more floppy bond angles are noticeably affected by the dynamics, i.e., by the finite temperature. From the $T = 300$ K simulations we estimated an average P−Ru−P bond angle close to 160°.

b. Ambient Temperature Molecular Dynamics of the Bisphosphine Complex (2). After energy minimization of the complex, a MD run at $T = 300$ K was started. No reaction was observed within the time-span of the MD simulation (600 fs). However, two particular observations may be worthwhile to note. First, whereas one of the Ru−P distances shows relatively small fluctuations around an average value of about 2.37 Å, after the initial 200 fs of simulation the other of the two Ru−P distances starts to exhibit fluctuations up to 0.15 Å (Ru−P varies between 2.2 and 2.5 Å). This suggests that one of the phosphines becomes less strongly bonded to the Ru center.

Second, during the simulation the carbene performed a full 180° rotation around the Ru=C bond. Although this rotation around the Ru=C double bond might seem a little surprising, it clearly supports the suggestion by Grubbs et al. who argued that in what they considered the most likely mechanism for the metathesis reaction to proceed (Scheme 6, pathway 2 in ref 18), a 90° carbene rotation is required in order to form the metallacyclobutane.

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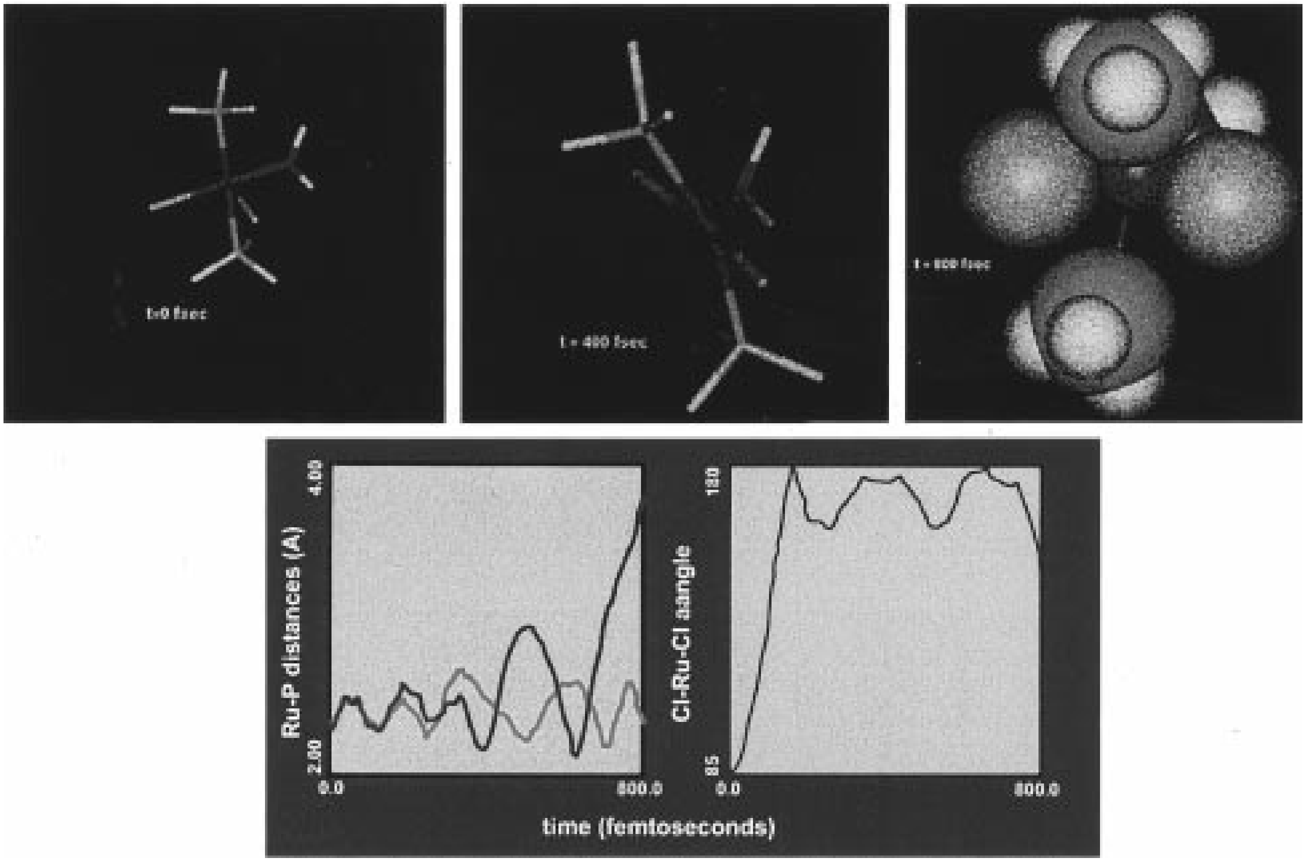

Figure 1. Snapshots of the $Cl_2(PH_3)_2Ru{=}CH_2$ bisphosphine complex taken during dynamics simulations performed at $T = 1273 \pm 600$ K. Timings in femtoseconds as indicated with the structures. The graphs illustrate the variation of the Ru−P distances and the Cl−Ru−Cl bond angle (90° = cis, 180° = trans) during the simulation. It is seen best from the right-hand snapshot that at this temperature the bisphosphine is unstable and readily splits off one of its phosphine ligands.

c. High-Temperature Simulations on Bisphosphine Complexes (1). The $Cl_2(PH_3)_2Ru{=}CH_2$ bisphosphine complex (no ethylene present) was studied at high temperatures, i.e., at $T = 1273\ K \pm 600$ K and at $T = 673 \pm 600$ K. The temperature indication means that, in the former case, the initial temperature is 1273 K, and fluctuations up to 600 K are allowed during the simulation. If the temperature starts to exceed the set temperature, temperature is reset to 1273 K by rescaling the atomic velocities. The initial structure had both phosphine groups in the axial positions and the chlorines in the cis configuration. Snapshots of the structures taken during the simulation are shown in Figure 1, along with graphs showing the variation of the relevant geometrical parameters. During the simulation at $T = 1273$ K, one of the phosphines leaves the ruthenium complex (see evolution of Ru−P distances and snapshots in Figure 1). This process is preceded by a transformation of cis-coordination of the chlorines toward a trans-coordination of the chlorine atoms (see Cl−Ru−Cl bond angle evolution in Figure 1). The carbene is able to exhibit large angle (up to 60°) librational motions around the Ru−C bond, as concluded after inspection of the time-dependence of the P−Ru−C−H dihedral angles. This simulation thus suggests that the monophosphine complex is readily formed at high temperature, i.e., in the high-end tail of the Maxwell−Boltzmann velocity distribution.

The same type of simulation performed at $T = 673$ K does not reveal debonding of a phosphine group within the timespan of the simulation. After a simulation of 800 fs there was no sign that decomposition would follow within the next few picoseconds, as otherwise corroborated from anomalous variations in internal bond lengths or bond angles. The Cl−Ru−Cl angle varied between the cis and the trans state during the simulation. As a consequence, this part of the first step in the pathway proposed by Grubbs et al. (see Scheme 1) will go with relative ease, whereas the dissociation of one of the phosphines requires a high temperature.

The two simulations, performed at $T = 673$ K and 1273 K, respectively, give evidence that the molecular species present in the high-velocity tail of the Maxwell−Boltzmann velocity distribution lead to dissociation of the bisphosphine. The fact that the molecules in the high-end tail of the Maxwell−Boltzmann distribution are unstable with respect to dissociation is in qualitative agreement with the experimental result of Grubbs et al.[18] that less than 5% of unbound phosphine is found in the reacting mixture. The transformation of cis to trans configuration of the chlorines was very evident from the simulation. However, this is not a priori in contradiction with the dominating pathway suggested by Grubbs, as the ethylene may positively influence the stability of the cis state. The substantial librational motion of the carbene supports the claimed[18] necessary rotation of this group preceding metallacycle formation.

d. High-Temperature Simulation on Monophosphine Complex (3). The same approach as applied in reaction 4.1.c on a bisphosphine complex was used to study the high-temperature stability of the Ru−P bond in the monophosphine complex. In this case we studied the monophosphine−ethylene complex, which may simultaneously show us some reactivity. Simulations were performed both at $T = 1273 \pm 600$ K and $T = 673 \pm 600$ K. During the simulations no chemical reactions were observed. At both temperatures the phosphine was seen

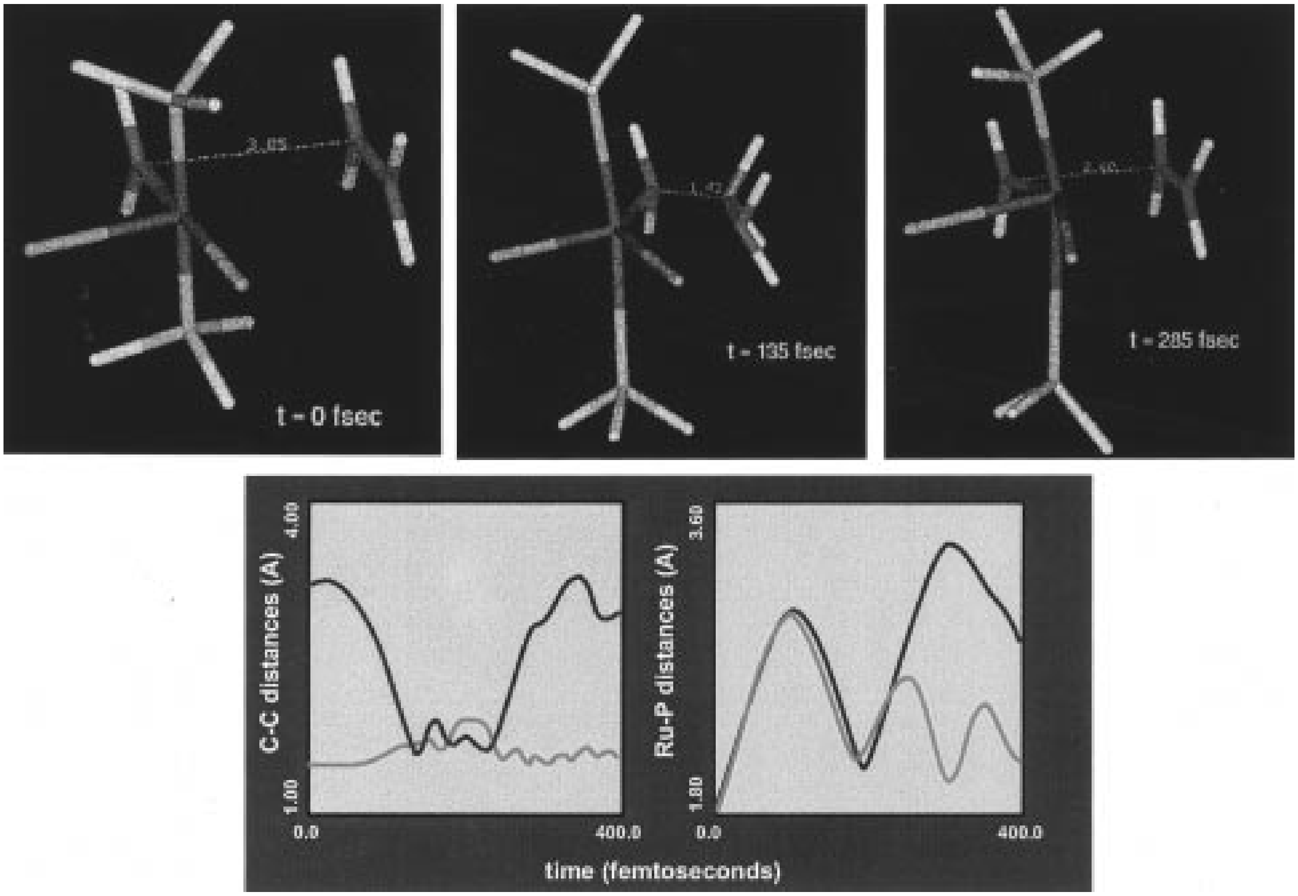

Figure 2. Results from the molecular dynamics simulation on the $Cl_2(PH_3)_2Ru{=}CH_2/C_2H_4$ bisphosphine system at $T = 400$ K. The initial geometry had a short Ru−P bond length of 1.86 Å. Insertion of ethylene is observed after 130 fs, but is found unstable in the following part of the simulation: see snapshots and the left-hand graph displaying the $C_{methyl}{-}C_{ethylene}$ and the internal ethylene C═C distance. The right-hand graph shows the Ru−P distances during the simulation.

to remain bonded to the ruthenium center, whereas the Ru−P bond length typically fluctuated between 2.1 and 2.6 Å. The configuration of the chlorines changes from trans (Cl−Ru−Cl = 180°) to an average bond angle of 145°. The carbene shows rotation around the Ru−C bond. At high temperature (1273 K) the rotation is constant during the simulation (with three rotations within the time-span of the current simulation). For the $T = 673$ K simulation the carbene rotates by 90°, with the dihedral angle P−Ru−C−H close to 90°. This conformation has one of the carbene hydrogen atoms pointing toward the ethylene, which prevents reaction of the Ru complex with the ethylene.

From the simulations reported thus far, we conclude that reactivity from the energy minimized complexes is unlikely, at least within the time-span of the simulations. The bisphosphine complex (**1**), however, turned out to be unstable at high temperature, and (one of) the Ru−P bond length tends to substantial fluctuation in most of the simulated systems. Even high-temperature simulations did not show chemical reactivity except for the loss of one phosphine in the bisphosphine complex. These high-temperature simulations have the kinetic energy within the molecule distributed over the various bonds. From these observations we concluded that selective bond activation seems the natural way to proceed and investigate reactivity of the Ru phosphines. In that case we do not simply look for molecules with sufficient kinetic energy to overcome an energetic barrier, but for the subset that has the kinetic energy in the appropriate bond for reactivity.

The observations from the high-temperature simulations reported above together with the recent evidence for high metathesis activity of the monophosphine complex reported by Grubbs et al.[18] suggest that the Ru−P bond in the bisphosphine complex is the most labile bond in the system. These bonds may thus be the easiest to induce vibrational excitation. In addition, deliberately putting excess kinetic energy in the Ru−P bond may provide us information on the effect of various type phosphines on the reactivity toward metathesis.

4.2. Molecular Dynamics Simulations Starting from Shortened Ru−P Bonds. We have subjected the bisphosphine complex (**2**) including the weakly coordinated ethylene to dynamics simulations starting from such geometries, with the initial Ru−P bond length at 1.8 Å. An MD simulation starting with this short Ru−P bond length involves a significant potential energy in the Ru−P bonds, which will be released as an increase in temperature during the simulation. The stored energy is so high that a straightforward dynamics simulation would lead to dissociation of both phosphine groups (we have confirmed this by actual simulation). To stimulate Ru−P debonding, but simultaneously prevent excessive and unrealistic heating of the system, simulations were performed in which the starting structure has the given short Ru−P distances, and the temperature was allowed to fluctuate within a certain given temperature window. Such a construction mimics different exchange rates of kinetic energy with the environment; i.e., it mimics part of the effect of a solvent. Whereas putting excess energy into a specific bond shows strong resemblance with forced motion

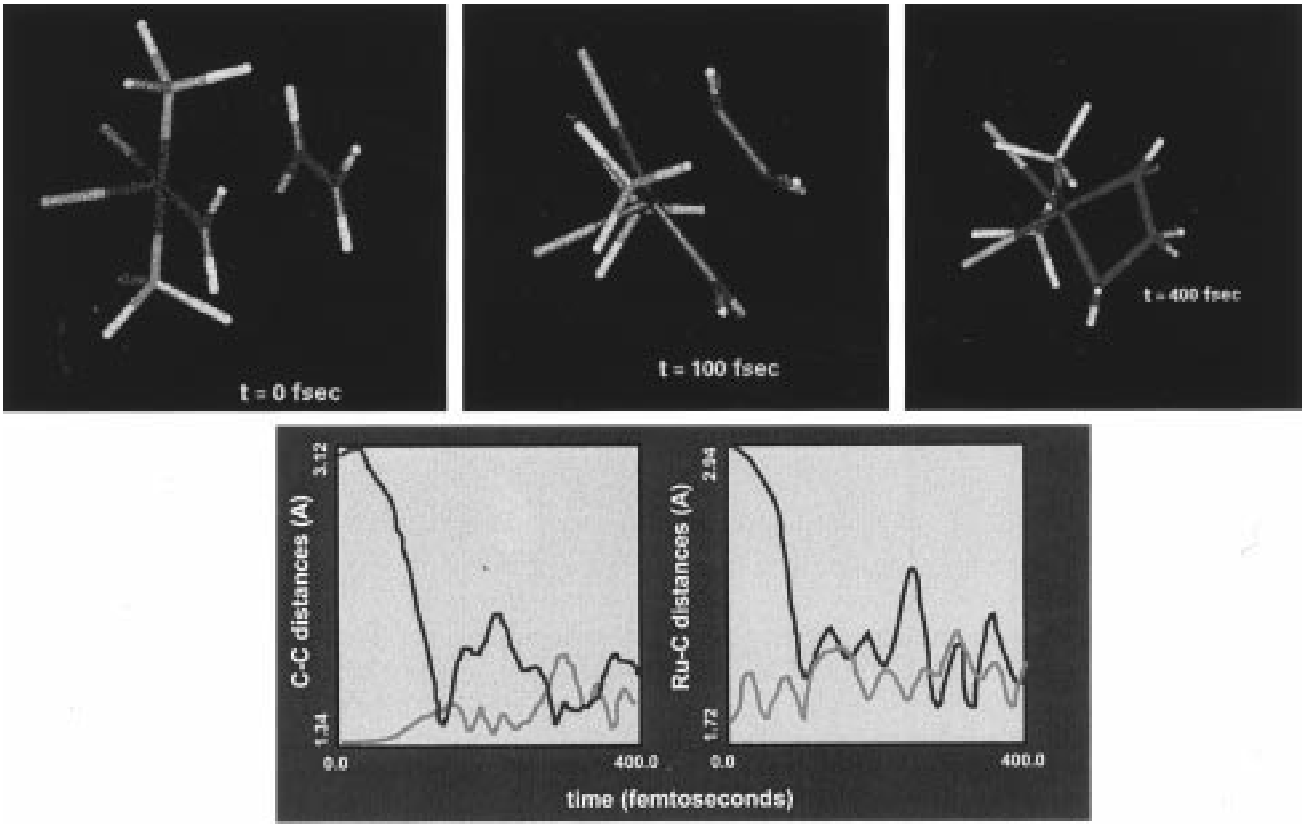

Figure 3. Results from the molecular dynamics simulation on the $Cl_2(PH_3)_2Ru{=}CH_2/C_2H_4$ bisphosphine system at $T = 400 \pm 250$ K. (Within the initial 30 fs the temperature control has reset temperature eight times). The initial geometry had a short Ru−P bond length of 1.86 Å. The *insertion of ethylene* is seen to occur after $t = 130$ fs, as is seen from the snapshots and the left-hand graph displaying the $C_{methyl}{-}C_{ethylene}$ and the internal ethylene C═C distance. A metallacyclobutane structure is formed, which is stable within the time-span of the simulation. The Ru−C(methylene) and one of the Ru−C(ethylene) bond lengths have become equal after a while, as seen from the right-hand graph, which agrees with the formation of a metallacyclobutane ring. During the entire simulation both phosphine ligands remain bonded to the Ru metal center.

along the reaction path (constrained MD simulation), in the latter case the entire reaction path has, in fact, already been prescribed. The former approach may still lead to different reactions, as we will indeed show. We start to discuss the simulations on the $Cl_2(PH_3)_2Ru{=}CH_2/C_2H_4$ bisphosphine system (**2**).

a. The $Cl_2(PH_3)_2Ru{=}CH_2/C_2H_4$ Bisphosphine System: MD Simulation at Constant Temperature: $T = 400$ K. In this simulation the temperature was maintained at 400 ± 40 K. The results of this simulation are shown in Figure 2. Insertion of ethylene is observed after 130 fs, but is found unstable in the following part of the simulation. In fact, ethylene insertion is annulled later in the simulation and the insertion reaction is seen to run backward, while the ethylene C═C double bond is reestablished. However, the Ru−C(methyl) and a Ru−C(ethylene) bond remain of the same length, indicating that the Ru has established bonding with two rather than one carbon atom. Apparently, the insertion process is unstable, but the Ru is capable of binding the ethylene.

b. The $Cl_2(PH_3)_2Ru{=}CH_2/C_2H_4$ Bisphosphine System: MD Simulation at $T = 400 \pm 250$ K. This simulation involves a starting temperature of $T = 400$ K, after which the temperature is allowed to vary by 250 K, that is between 150 K and 650 K. Within the initial 30 fs the temperature control has reset temperature eight times. After that, temperature did not exceed it set boundary values of 150 and 650 K. This implies that the system, while showing possible reactivity, is not exposed to unphysical temperatures. Thus, specific features seen in the simulation after 30 fs are not an unintended consequence of temperature resetting in that time span. The results of the simulation are shown in Figure 3. The *insertion of ethylene* is seen to occur after $t = 130$ fs. A metallacyclobutane structure is formed, which is stable within the time-span of the simulation. The Ru−C(methylene) and one of the Ru−C(ethylene) bond lengths have become equal after a while, which agrees with the formation of a metallacyclobutane ring. During the entire simulation both phosphine ligands remain bonded to the Ru metal center.

c. The $Cl_2(PH_3)_2Ru{=}CH_2/C_2H_4$ Bisphosphine System: MD Simulation at $T = 400 \pm 500$ K. This simulation involves a starting temperature of $T = 400$ K, after which the temperature is allowed to vary between 0 and 900 K. Within the initial 30 fs the temperature control has reset temperature four times. After that, temperature did not exceed its set boundary values of 400 and 900 K. The results of this simulation are shown in Figure 4. When we look at the overall time-evolution of the C(methylene)−C(ethylene) and the C(ethylene)−C(ethylene) distances, as shown in the left-hand graph of Figure 4, we note that this simulation reveals a *pure metathesis reaction*: there is a switch of the ethylene double bond from two of the three carbons to another set of two carbons in the system. Similar switching behavior is observed regarding the $Ru{-}C(H_2)$ distances, viz. the right-hand graph in Figure 4.

d. The $Cl_2PH_3Ru{=}CH_2/C_2H_4$ Monophosphine System. It has been suggested that the active species in the metathesis is a monophosphine complex.[18] We therefore wanted to test whether a metathesis reaction could be simulated for the $Cl_2PH_3Ru{=}CH_2/C_2H_4$ *mono*phosphine system.

A summary of the results of the simulation, which was performed microcanonically (initial temperature $T = 0$ K, and then temperature may evolve freely, with the energy of the

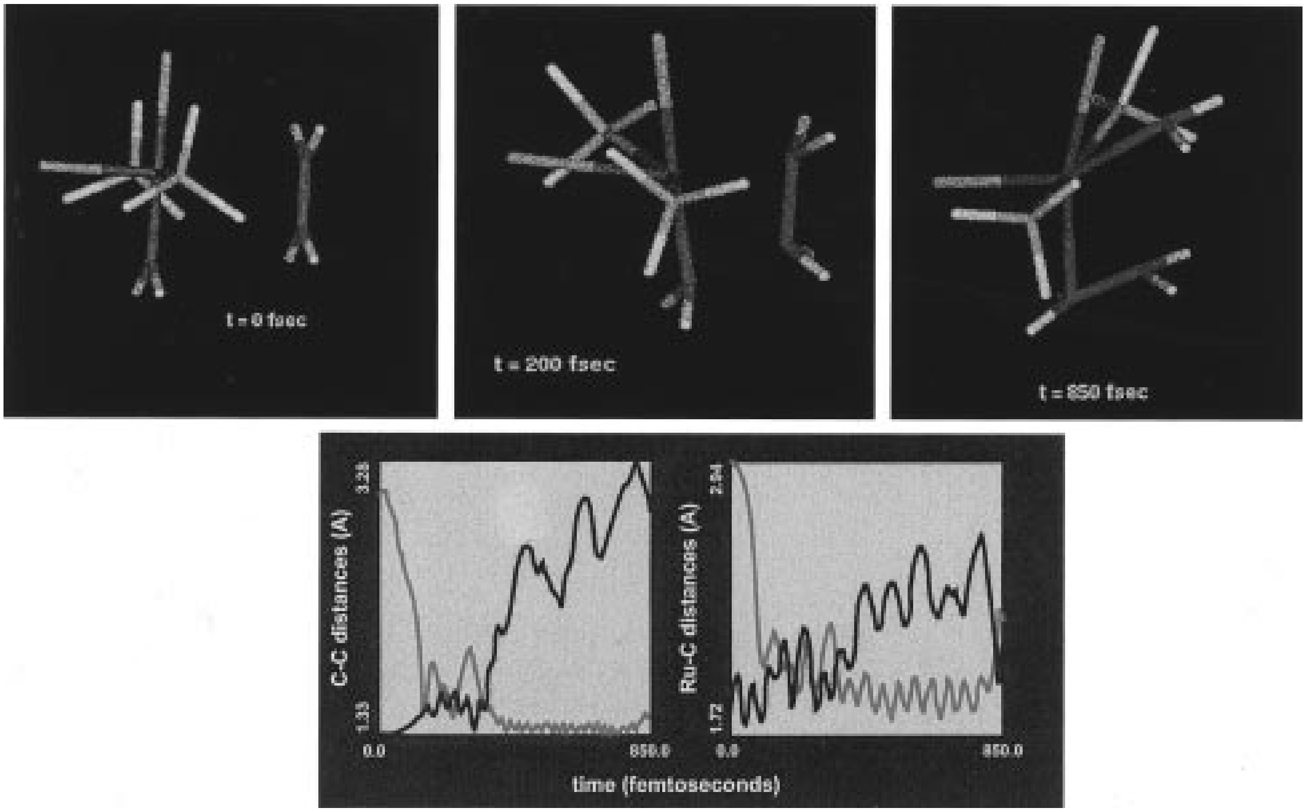

Figure 4. Results from the molecular dynamics simulation on the $Cl_2(PH_3)_2Ru{=}CH_2/C_2H_4$ bisphosphine system at $T = 400 \pm 500$ K. (Within the initial 30 fs the temperature control has reset temperature four times). The initial geometry had a short Ru−P bond length of 1.86 Å. A pure *metathesis reaction* is observed for this case, as is most evident from the two graphs. The left-hand graph illustrates the reversal of the two relevant C−C distances (the ethylene C=C distance and one of the $C_{methylene}{-}C_{ethylene}$ distances), whereas the right-hand graph displays the reversal of the Ru−C distances accompanying metathesis.

system constant throughout the simulation), is shown in Figure 5. It is directly observed that the simulation reveals a *pure* metathesis reaction: there is a switch of the ethylene double bond from two of the three carbons to another set of two carbons in the system. Similar switching behavior is observed regarding the Ru−C(H_2) distances. The temperature rise in this simulation did not exceed 1000 K.

5. An Explanation for the Effect of Phosphine Ligands on Reactivity

A further result can be abstracted from the simulations presented. Both room-temperature and high-temperature simulations starting from equilibrium Ru−P bond lengths (∼2.35 Å) did not show any chemical reaction progress. No reaction was observed despite the fact that the simulations were started from a geometry having the proper relative orientation of the molecules with respect to each other to allow for direct reaction (in other words, the relative orientation of the reactive orbitals is correct). On the contrary, all simulations which started from shortened Ru−P bonds, and thus had the excess kinetic energy concentrated in specific bonds, revealed some sort of chemistry, either metathesis, insertion, or metallacyclobutane formation. In all simulations that showed a chemical reaction, the Ru−P bond length was over 2.65 Å in the first stage of the simulation. We conclude from this and from the experimental observation reported by Grubbs et al. that the monophosphine is much more reactive than the bisphosphine, that the Ru−P bond has to breath in order to either provide space or positively influence the electronic structure on the Ru center in order to have a chemical reaction proceeding. This explains the well-known experimental observation that Ru complexes with small, nonsteric or poor donating, phosphine ligands exhibit relatively low activity, while larger, donating, phosphines such as the cyclohexyl substituted phosphines have a much higher activity. With sterically larger ligands, the equilibrium Ru−P distances is elongated compared to the sterically minimal ligands (e.g., PH_3), and thermal fluctuations will more easily drive the Ru−P beyond the limit for chemistry to occur (more than the previously mentioned 2.65 Å). The fact that larger phosphines will lengthen the equilibrium bond length may be corroborated from a comparative list of Fe−P bond lengths.[25] In addition, it is an experimental observation that the rate of metathesis increases with temperature, which we can thus rationalize by recognizing an increasing fraction of molecules in the high-end tail of the Maxwell−Boltzmann velocity distribution with increasing temperature.

In addition, a necessity for the Ru−P bond to lengthen considerably to allow for a chemical reaction to proceed also explains the much higher activity of the monophosphines compared to the bisphosphines as experimentally demonstrated by Grubbs et al. The lengthening of the Ru−P bond is more than the bond length fluctuation due to a normal vibrational mode. As a consequence, the energy to be stored in the Ru−P bond in order to lengthen it beyond 2.65 Å has to be built up in the course of time. However, the accumulation of surplus kinetic energy may occur in one Ru−P bond, but it will also flow out of that bond by the same vibrational coupling mechanisms through which it was established. The magnitude of the lengthening will thus only be accomplished accidentally, and is expected to be relatively short-lived. Because for the bisphosphine the argument of bond lengthening in order to

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[25] Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1990**, *9*, 1758−1766.

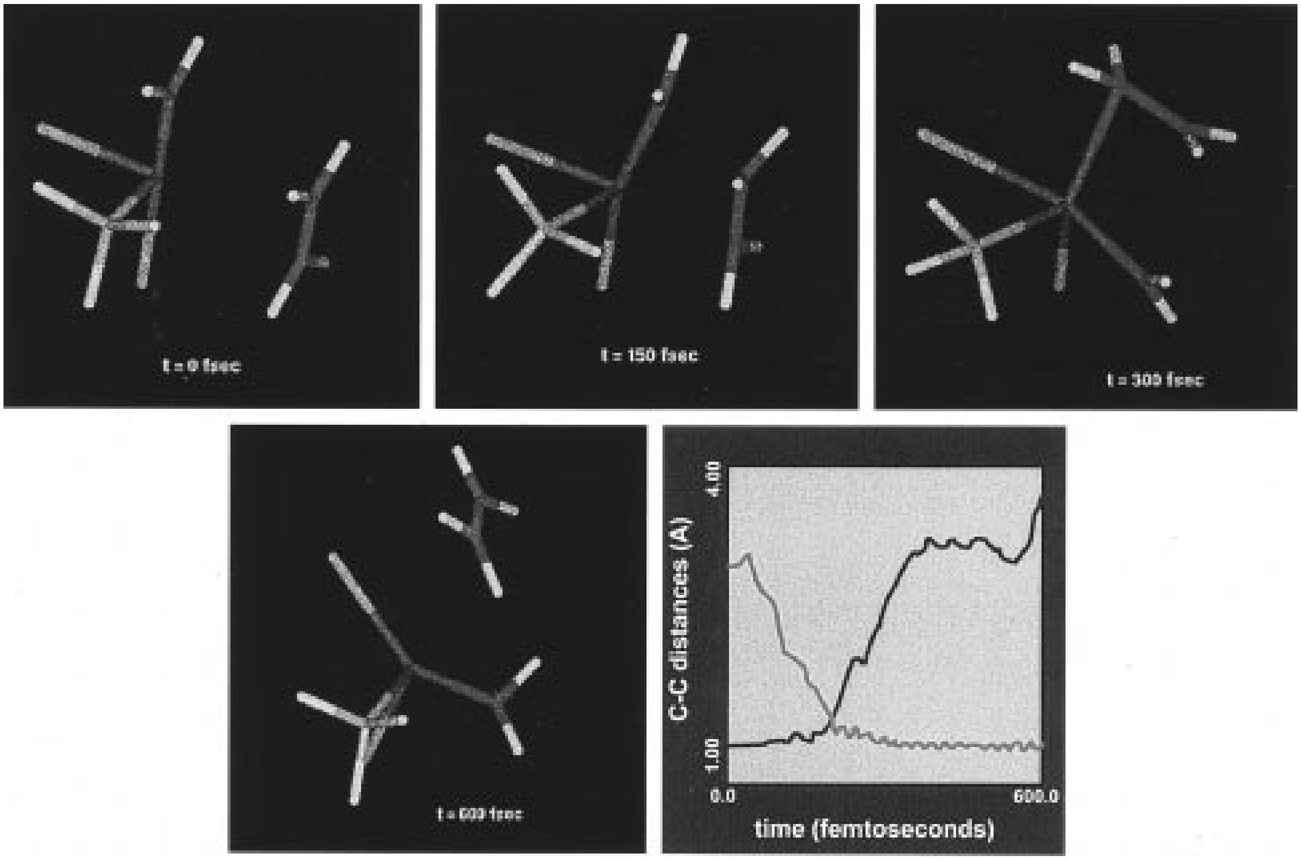

Figure 5. Results from the molecular dynamics simulation on the *mono*phosphine $Cl_2PH_3Ru{=}CH_2/C_2H_4$ complex starting at $T = 0$ K and during which temperature was allowed to evolve freely. The initial geometry had a short Ru−P bond length of 1.86 Å. The snapshots show that a pure *metathesis reaction* is observed. This is more clearly illustrated in the graph in which the time evolution of the $C_{methyl}{-}C_{ethylene}$ and the internal ethylene C═C distance are displayed.

observe a chemical reaction appears (see the results from our simulations) to apply to both phosphines, a surplus of kinetic energy has to be present *in both Ru−P bonds at the same time*. When this surplus of energy is accidentally present in one of the phosphines, it will be present with very low probability in both phosphines at the same time. Qualitatively this explains the observation by Grubbs et al. that the monophosphine dominates the reactivity despite the fact that its concentration is less than 5% of the total concentration of ruthenium−phosphine complex present in the reaction mixture. Further dynamics simulations on ruthenium−phosphines with larger ligands may be performed to provide further evidence.

6. Conclusions

In this study two things have been accomplished. First, from a simulation point of view, it was shown that different chemistry can be studied by varying the absolute temperature and the set range of temperature fluctuations allowed in the simulation. In the present set of simulations the latter parameter (temperature window) was shown to primarily set the initial excess kinetic energy in the Ru−P bonds, whereas in the main part of the simulations this window acts as a heat bath (as in classical molecular dynamics simulations) which should be interpreted as a measure for the exchange rate of kinetic energy (heat) between the reaction species (solute) and the environment (solvent). This type of simulation is different from the quantum simulations on chemical reactions reported so far, which tend to trace down a specific presumed reaction path and, therefore, a specific preset type of reaction. It is unnecessary to say that more studies are needed to provide a more detailed link, e.g., in terms of solvent quality, between these calculations and the real, experimental, system.

Second, in this study we focused on the chemical activity of a ruthenium−phosphine catalyst toward ethylene. Depending on temperature conditions set in the MD simulation, the interaction of a ruthenium−phosphine catalyst with ethylene revealed insertion, the formation of a metallacyclobutane, or a pure metathesis reaction. A comparison with recent experimental results from Grubbs et al.[18] shows that some of the preliminary interpretation presented in that work is supported by the present calculations. First, whereas in the crystal structure the Cl−Ru−Cl is in the trans configuration, the mechanism proposed by Grubbs (see Scheme 1) requires trans−cis configurational exchange. We have observed that this exchange is facile, even at room temperature. In the next step of Grubb's proposed mechanism, the carbene needs to rotate, and a phosphine preferably debonds. Carbene rotation was indeed observed in several of our simulations, as well as the loss of a phosphine at high temperature. Grubbs also reports the activity of the bisphosphine, which agrees with our simulations. The metallacyclobutane form is also established as an intermediate, and metathesis was observed when selective bond activation was imposed. Therewith we have revealed and lend support to the individual steps in the mechanism proposed by Grubbs viz. Scheme 1.

Furthermore, the simulations provide direct evidence that energy stored in the Ru−P bond, or otherwise the lability of the Ru−P bond, is of crucial importance for the metathesis reaction to proceed. The requirement to store excess energy in the Ru−P bonds in order to allow for chemical reactions to proceed (metathesis, insertion, or metallacyclobutane formation) explains the high activity of the monophosphine system compared to the bisphosphines, and the higher activity of sterically larger ligands compared to the sterically minimal ligands such as PH_3. Thus, our simulations have provided a qualitative picture for the high activity of the monophosphine catalyst which is in agreement with the experimental data presented by Grubbs et al. The computed data thus partly confirm the reliability of the present simulations and/or provide further evidence for the mechanism proposed by Grubbs.

Finally, it must be emphasized that, although we feel that the current approach opens a new field for using Car–Parrinello type simulations to explore chemical reactions, much more work is needed to explain in detail reaction mechanisms in specific cases such as the ruthenium-based metathesis reaction discussed in the present paper. Nevertheless, despite the need for more extensive work, the current simulations have already delivered results which could be compared in a useful way with the recent experimental data reported by Grubbs et al.

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