

First principles molecular dynamics applied to homogeneous catalysis: on ethylene insertion mechanisms and metathesis

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Abstract

We have summarized part of our work involving first principles molecular dynamics simulations on organometallic-based homogeneous catalysts. Explicit dynamics effects can be uniquely extracted from such simulations, and related to structure and reactivity. Examples given deal with metallocene-based ethylene polymerisation, ethylene insertion in a platinum hydride, and olefin metathesis. The dynamics simulations in particular reveal information on the flexibility of these molecular systems, and elucidate mechanistic details (e.g., relevance agostic interaction). For the Ru-based metathesis catalyst an alternative simulation approach has been applied, which has enabled us to make detailed comparison between simulation results and the reaction mechanism proposed by Dias et al. [E.L. Dias, S.T. Nguyen, R.H. Grubbs, *J. Am. Chem. Soc.* 119 (1997) 3887], showing 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 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 Dias et al. can be understood. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Over the last decennium considerable progress has been made in the computational chemistry field, which now allows for the calculation, at the full quantum mechanical level, of realistic structures of both homogeneous and heterogeneous catalysts. This new stage has been

accomplished through a combination of speed-up and quality improvement in computer hardware, software, and last but not least theoretical method development. Consequently, we have seen a considerable number of theoretical papers in the scientific literature over the last years, a number that is still growing.

The computational chemistry field can, in terms of the way of describing interatomic potential, be roughly divided in three clusters: the force field approach, semi-empirical quantum mechanics (Hückel, MNDO, AM1, etc.), and ab

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initio or first principles quantum mechanics. The latter involves brute force solution of the Schrödinger equation. The first two of these usually lead to reasonable geometries for organometallic species, but there are generally problems related to the energetics. However, these methods may be used as pre-optimizer before starting *ab initio* work (although even then considerable care is required), or applied to deal with specific purpose, e.g. the evaluation of bite-angles.

One of the more recent developments is the application of the first principles Car–Parrinello molecular dynamics method [1] in chemistry. One of the early reports on application to chemical reactivity was a 1994 paper on metallocene-based ethylene polymerisation [2]. This method is based on density functional theory, nowadays a very popular method in the study of many electron systems in both chemistry and solid-state physics. The electrons are treated fully quantum mechanically, the nuclei are treated classically in most current programmes. The attractiveness of this method in the study of chemical reactions lies in the fact that a chemical reaction inherently involves atoms moving, and the wavefunction changes upon reaction. Therefore, a simulation technique comprising both nuclear dynamics and treating the electrons quantum mechanically seems the most appropriate tool for such an exercise. Because the Car–Parrinello method is based on a plane-wave basis set rather than the traditional localised orbital (1s 2s, 2p, . . . , etc., functions) basis, there has been some skepticism among chemists on the appropriateness of such a basis set for molecular calculations and its relative accuracy. We recently showed that very similar activation energies are obtained for an aluminium-based catalyst system when comparing Car–Parrinello results with traditional localised orbital calculations [3]. For density functional theory (DFT), however, despite its advantages and computational efficiency, the choice of the functional in terms of gradient corrections in particular remains an issue of considerable im-

portance. Different gradient correction schemes, and hybrid methods like B3LYP (which mix some of the Hartree–Fock energy into the DFT energy), may yield non-negligible differences in relative energies, and therefore different relative stabilities, reaction enthalpies and activation energies for chemical systems. Moreover, experience has shown that some properties are in fact excellently calculated at the LDA level (which is the basic DFT without gradient corrections), whereas some other properties can only be evaluated accurately with such corrections incorporated in the calculations. Nevertheless, currently there is no scheme that yields correct relative energies. Computationally, for the most accurate energies one still has to rely on very expensive, mostly entirely unfeasible, post-Hartree–Fock methods such as coupled cluster and multiconfigurational methods.

Having said that, we have taken the point of view that rather than focussing on accurate energetics, which we believe is unfeasible for the reasons just mentioned, it is more appropriate to try and investigate the general mechanistic features of chemical reactions in general in order to provide the experimental chemist with general concepts and ideas on reactions and reaction mechanisms. Moreover, simulations with that aim can be used to investigate already suggested mechanistic aspects, and thus make a direct link with the work of the bench chemist. Although the outcome of such simulations is obviously also affected by the quality of the theoretical method, i.e. in the present case the DFT variant, general mechanistic features can be recovered. More precise statements about the onset of phenomena as a function of, e.g., temperature are not possible because of their dependence on the quality of the generated energy values.

In this contribution we first review some of our earlier findings on homogeneous catalysts based on first principles simulations, with emphasis on the dynamics aspects. Next, after a brief description of the calculation details (Section 3), we summarize our recent theoretical work on the bisphosphine $\text{Cl}_2(\text{PH}_3)_2\text{Ru}=\text{CH}_2$

complex and its monophosphine equivalent which were taken as model compounds for the Grubbs catalyst [4].

2. Explicit dynamics in homogeneous catalysis from MD simulation studies

Dynamics simulations are particularly useful to study the flexibility, or stiffness, of molecular systems. Full first principles calculations inherently take account of anharmonicity in the potential (again, precise effects will depend on the quality of the quantum mechanical method employed, basis set size, etc.), and temperature can be set explicitly to study systems at more realistic conditions than zero Kelvin as in static quantum mechanical calculations. Here we summarize some of our earlier findings.

There are several theories which could describe olefin polymerisation, with those due to Cossee [5] and Brookhart and Green [6] well-known. The latter involves agostic interaction in the insertion process. This is what was investigated by MD simulations [2,7]. Fig. 1 displays on the left hand side the reaction profile in the form of the internal ethylene C=C bond length and the distance between one of the ethylene carbon atoms and the methyl carbon bonded to the metal centre in $(\text{SiH}_2)\text{Cp}_2\text{ZrCH}_3(\text{C}_2\text{H}_4)^+$, revealing insertion of ethylene after some 150 fs. The right-hand side plot of Fig. 1 displays the Zr–H distances for all three methyl hydrogens as a function of time. Note that an agostic interaction, characterised by one very short Zr–H distance, is formed prior to ethylene insertion. This phenomenon has been observed consistently in series of simulations on Ti and

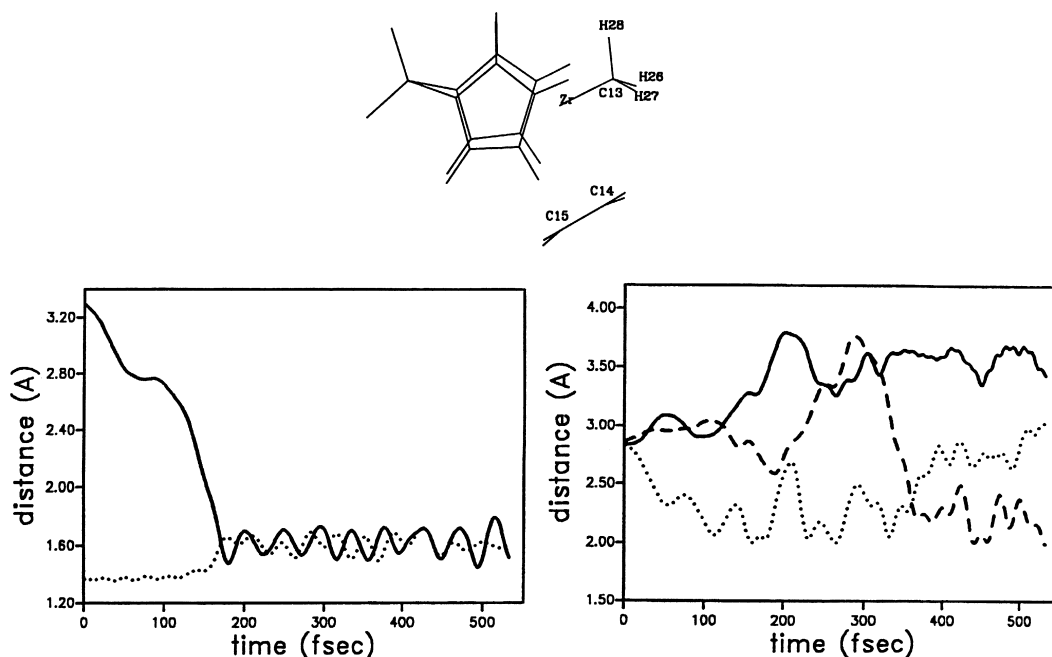


Fig. 1. Structure of the $(\text{SiH}_2)\text{Cp}_2\text{ZrCH}_3(\text{C}_2\text{H}_4)^+$ complex. Left-hand side plot: Time evolution of the methyl/ethyl C–C distances during the molecular dynamics simulation. The solid curve represents the distance between the methyl carbon atom and the nearest ethylene carbon atom (C13–C14). The broken line represents the ethylene internal C–C bond length (C14–C15). Right-hand side plot: Time evolution of the distance between the Zr atom and each of the three hydrogen atoms belonging to the methyl group (the original methyl group bonded to the Zr). The time evolution of one of the hydrogen atoms depicted by the dotted curve shows the development of α -H agostic interaction. Later on in the simulation (after about 450 fs) one of the other protons (broken curve) exhibits γ -H agostic interaction.

Zr-based metallocenes [2,7]. Another possibly noteworthy aspect revealed from these simulations is the flexibility of the bis Cp system. Whereas one may anticipate that the valence orbital system of the Cp rings may have strong interaction with the metal's d orbitals and therefore the Cp rings may be tightened to the metal centre, Fig. 2 shows significant fluctuations in the Si–C–Cp angle.

Contrary to this bis-Cp metallocene case, the P–Pt–P angle in the (H)Pt(PH₃)₂–C₂H₄ complex was found to show very little variation despite the openness of this structure [8]. This is illustrated in Fig. 3.

These examples illustrate the potential of first principles dynamics simulations to show explicit dynamics effects and their relation to flexibility and stiffness of molecular species. Moreover, also in a crystal structure atoms vibrate, and static structure minimisations might therefore lead to different valence or torsional angles as corroborated from experimental crystallographic data. An example is the model structure for the Grubbs catalyst, Cl₂(PH₃)₂Ru=CH₂, a system we will discuss in more detail in Section 4. Experimental crystallographic studies on related species give a value for the P–Ru–P bond around 167°, whereas a static minimisation gave 180°. A finite temperature simulation at $T =$

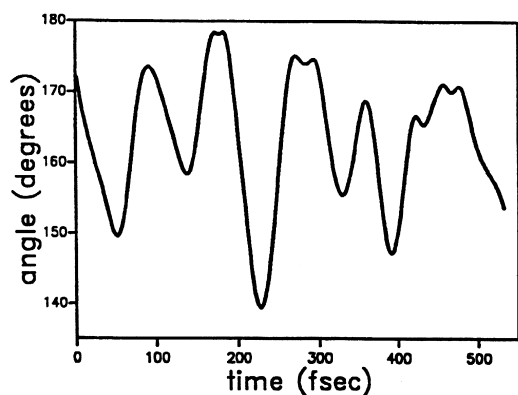


Fig. 2. Time evolution of the Si–C–Cp angle in the (SiH₂)Cp₂ZrCH₃(C₂H₄)⁺ system, where the coordinate taken for the Cp ring is the centre of gravity of the ring.

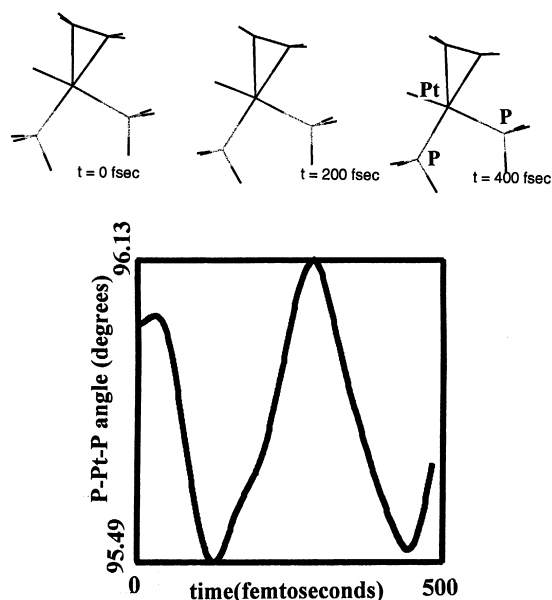


Fig. 3. Time evolution of the (H)Pt(PH₃)₂–C₂H₄ complex during the molecular dynamics simulation. Shown are snapshots of the molecular structure during simulation, and a graph displaying the variation of the P–Pt–P angle, which is very small despite the very open structure of the species compared to the metallocene complex of Figs. 1 and 2.

300°C revealed an average P–Ru–P bond angle of 160° [9].

3. Computational details for Ru-metathesis simulations

For a description of the soft- and hardware employed, and for aspects of the simulations, we refer to Refs. [2,7,9]. Vanderbilt-type pseudopotentials have been used, for ruthenium the valence electrons treated explicitly included 4s²4p⁶4d⁷5s¹. An energy cut-off of 25 Ry was employed for the plane-wave expansion. Gradient corrections according to Perdew [10] and Becke [11] were included. Before starting a molecular dynamics simulation, the molecular structure was energy minimized using a steepest descent routine, except for simulations starting with excess energy in the Ru–P bond(s) [9].

4. Olefin metathesis with the Grubbs catalyst: a simulation study

Recently, olefin metathesis has attracted considerable attention, both for the reasons of fundamental scientific interest as well as with regard to potential practical applications [12]. In a very interesting recent paper, Dias et al. [4] presented experimental data including a detailed study on the catalyst $\text{Cl}_2(\text{PCy}_3)_2\text{Ru}=\text{CHPh}$ 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 the scheme below (Scheme 1). In the following part we will discuss the issue of the presence and activity of the monophosphine complex. Further results on the bisphosphine equivalent can be found elsewhere [9].

Our strategy in the study on the Grubbs Ru-based metathesis catalyst, that is on the model species $\text{Cl}_2(\text{PH}_3)_2\text{Ru}=\text{CH}_2$ for that catalyst and its monophosphine counterpart $\text{Cl}_2\text{PH}_3\text{Ru}=\text{CH}_2$, has not been by probing the reaction path by constraining a reaction coordinate as normally practised in both static as well as dynamics simulations of catalytic chemical reactions. Our alternative approach is based on the following considerations. Molecules undergo a chemical reaction when they have sufficient energy to overcome the activation energy for that reactive process. In an ensemble of

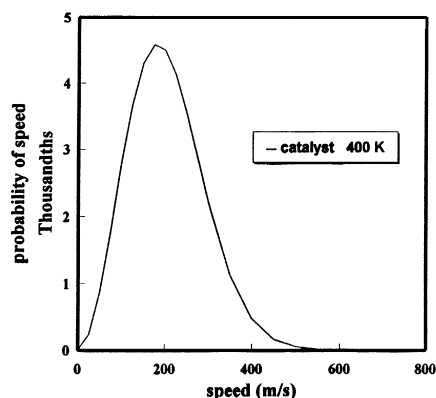
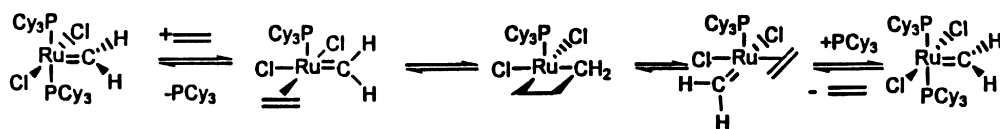


Fig. 4. Maxwell–Boltzmann distribution of molecular speeds for a typical organometallic species and $T = 400$ K.

molecules the molecular speeds show a Maxwell–Boltzmann distribution. For the molar mass of a typical homogeneous catalyst like discussed in this paper, and a temperature of $T = 400$ K, this distribution looks as depicted in Fig. 4. Here we see that there is a non-negligible fraction, say close to 1%, that has a speed 2–2.5 times the average speed, and therefore four to six times the kinetic energy of the average species. Translated into the situation of simulating a single molecule, this implies that some molecules act as if they would have a temperature four to six times the given average temperature. Consequently, dynamics simulations at $T = 800$ – 1200 K could tell us something about the chemistry of the molecules in the high-end tail of the Maxwell–Boltzmann molecular speed distribution.

We have applied this approach to the bisphosphine complex $\text{Cl}_2(\text{PH}_3)_2\text{Ru}=\text{CH}_2$. Individual simulations were performed at $T = 873$, 1073 and 1273 K. Results are shown in Fig. 5. Note the strong fluctuations in the Ru–Cl distances, and the relative easy of the configurational ex-



Scheme 1.

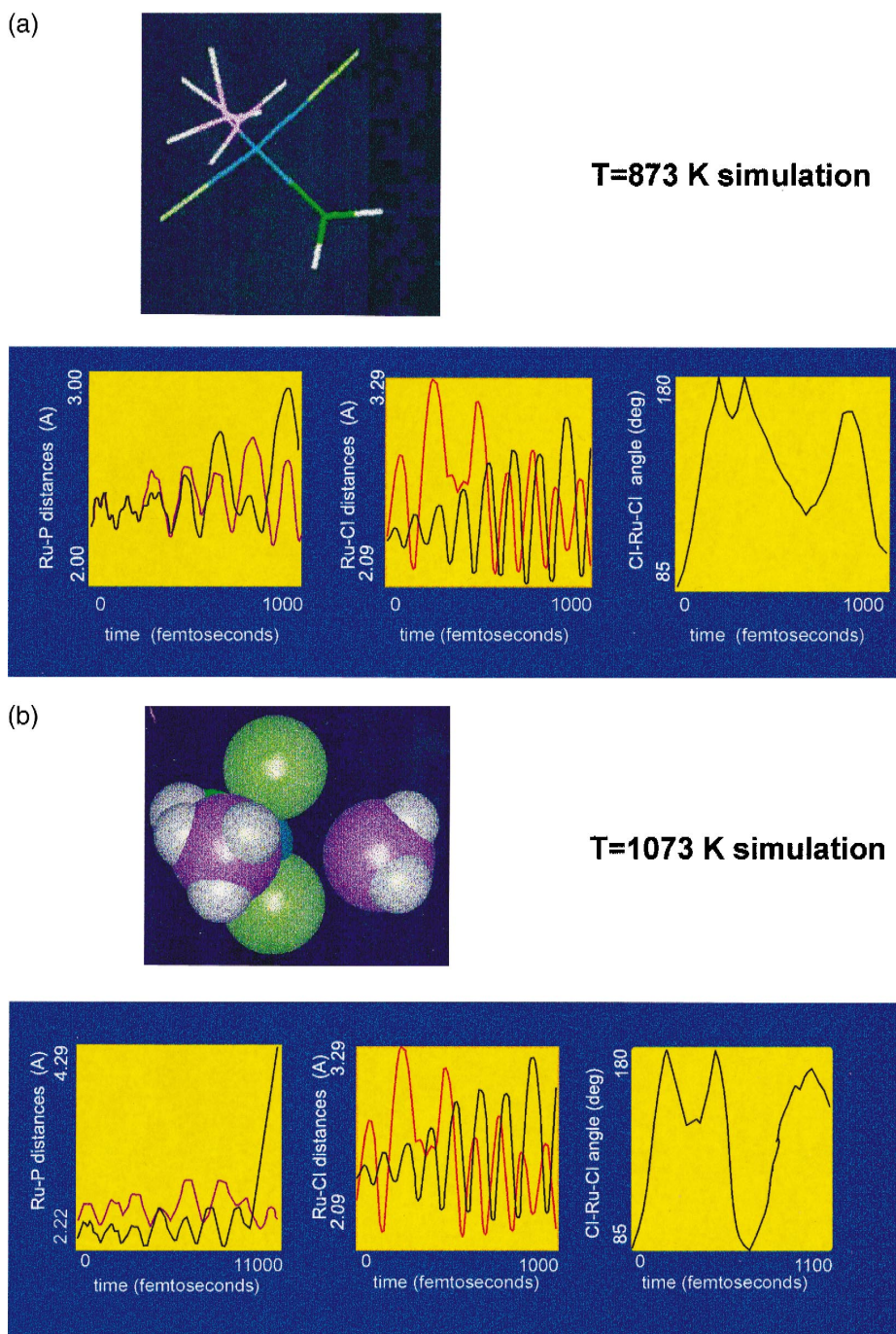


Fig. 5. Snapshots of the $\text{Cl}_2(\text{PH}_3)_2\text{Ru}=\text{CH}_2$ bisphosphine complex taken during dynamics simulations performed at $T = 873$, 1073 and 1273 K respectively. Timings in femtoseconds as indicated with the structures. The graphs illustrate the variation of the Ru–P and Ru–C distances and the Cl–Ru–Cl bond angle ($90^\circ = \text{cis}$, $180^\circ = \text{trans}$) during the simulation. The 1073 and 1273 K plots show that at sufficiently high temperature, or better stated for sufficiently high internal energy, the bis-phosphine is unstable and readily splits off one of its phosphine ligands.

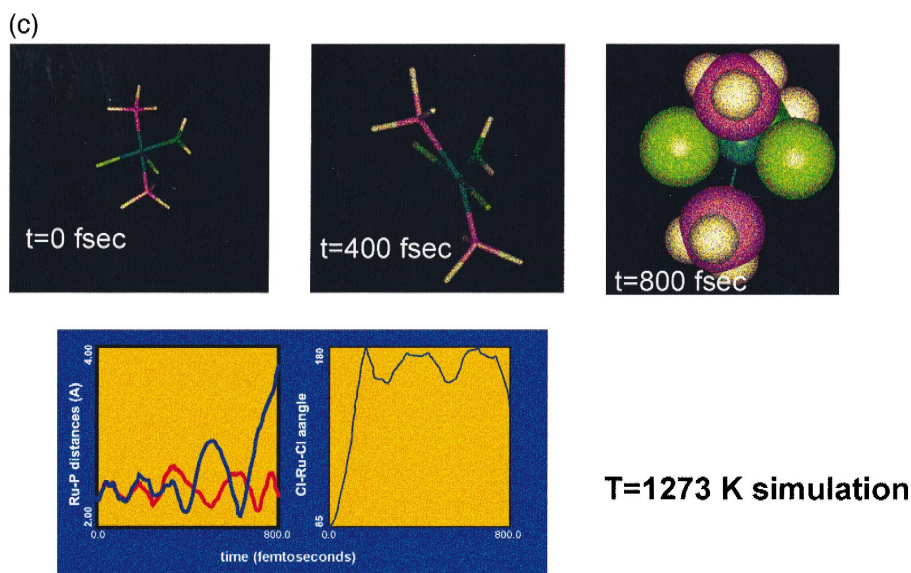


Fig. 5 (continued).

change between *cis* and *trans* for the Cl–Ru–Cl triple [4]. The latter was a prerequisite for the reaction scheme proposed by Dias et al. [4] to apply. The 1073 and 1273 K plots show that at sufficiently high temperature, or better stated for sufficiently high internal energy, the bisphosphine is unstable and readily splits off one of its phosphine ligands. This shows that these simulations at least qualitatively reveal the observation reported by Dias et al. [4] that a few per cent of the species is in the monophosphine form. Moreover, based on this information we have a qualitative explanation for the high activity, as reported by Grubbs, of the monophosphine form compared to the bisphosphine complex. As revealed from simulations on the bisphosphine species [9], considerable surplus energy is required in the Ru–P bond in order to have metathesis reactions proceed. High energies in a specific bond are realistic, although only expected in the far high-end of the Maxwell–Boltzmann distribution, and will therefore be experienced by relatively few molecules only. For the bisphosphine, reaction requires an enhancement of the energy in the P–Ru–P stretch vibrations which is significantly larger than the enhancement required for

the single Ru–P bond in the mono-phosphine complex. The consequence that excitation of a single Ru–P bond in the monophosphine is much more likely than excitation of P–Ru–P in the bisphosphine, qualitatively explains the high reactivity of the monophosphine compared to the bisphosphine, although its abundance is much lower.

That the monophosphine is active in metathesis was shown from dynamics simulations providing sufficient excess energy is available in the Ru–P bond, viz. Fig. 6. Similar conclusions could be drawn from simulations on the corresponding bisphosphine [9]. In summary, our dynamics simulations on both the mono- and bisphosphine complexes revealed and lend support to the mechanism proposed by Dias et al. [4]. 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 is confirmed by the present simulations. Starting from the observation that selective bond excitation is necessary

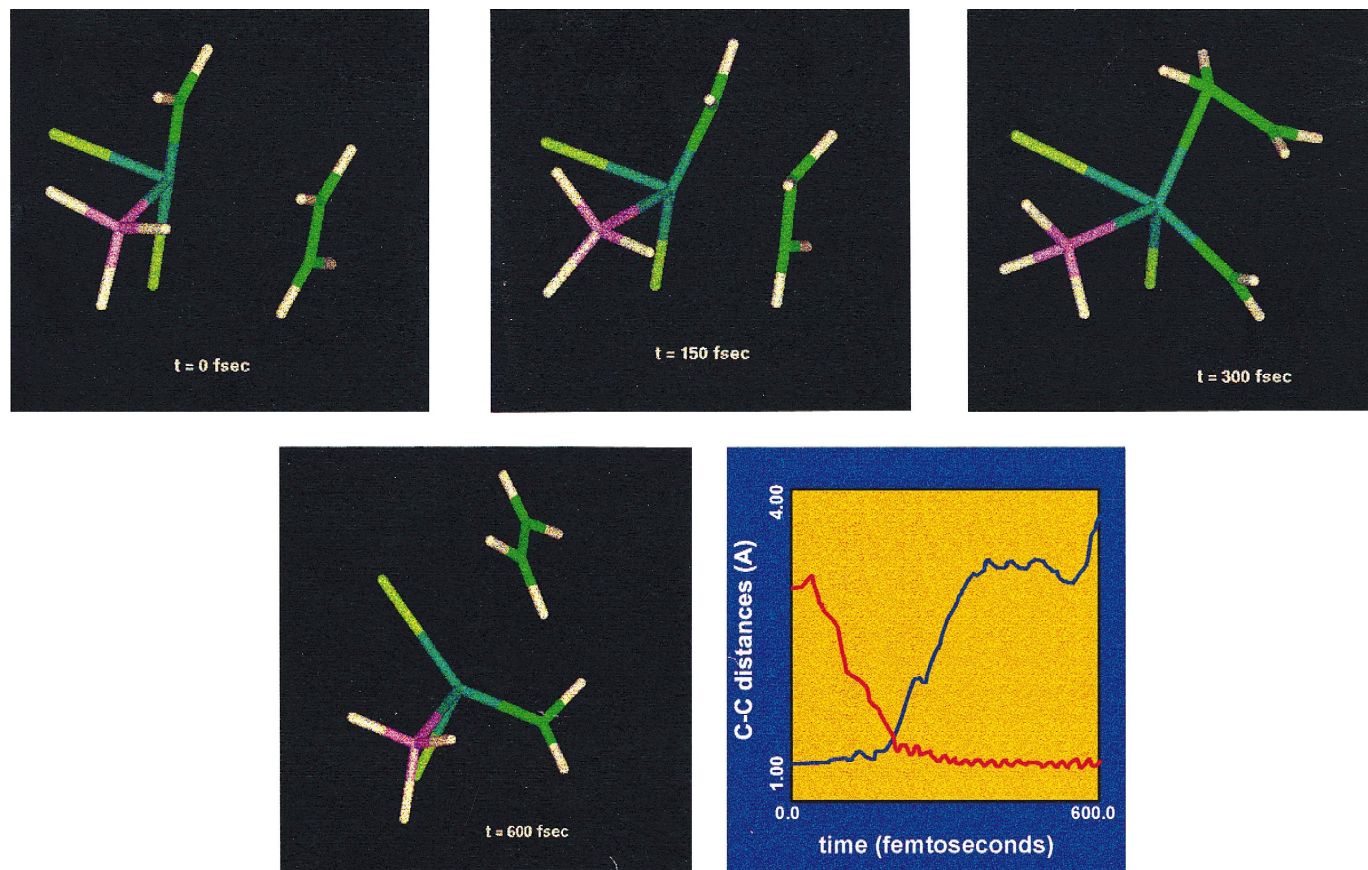


Fig. 6. Results from the molecular dynamics simulation on the monophosphine $\text{Cl}_2\text{PH}_3\text{Ru}=\text{CH}_2/\text{C}_2\text{H}_4$ complex starting at $T = 0$ K and during which temperature was allowed to evolve freely. The initial geometry had a short Ru–P bond length of 1.86 Å as a way of introducing excess energy in this bond. 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 $C_{\text{methyl}}-C_{\text{ethylene}}$ and the internal ethylene $C=C$ distance are displayed.

to exhibit reactivity, the higher activity of the monophosphine system compared to bisphosphine complexes reported by Dias et al. [4] 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 gives higher metathesis activity, can be rationalized by their intrinsically more labile Ru–P bonds as indicated by longer Ru–P bond lengths.

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