

Mechanism and Activity of Ruthenium Olefin Metathesis Catalysts: The Role of Ligands and Substrates from a Theoretical Perspective

Christian Adlhart and Peter Chen*

Contribution from the *Laboratorium für Organische Chemie, Swiss Federal Institute of Technology, ETH Zürich, CH-8093 Zürich, Switzerland*

Received October 6, 2003; E-mail: chen@org.chem.ethz.ch

Abstract: The reaction mechanism of olefin metathesis by ruthenium carbene catalysts is studied by gradient-corrected density functional calculations (BP86). Alternative reaction mechanisms for the reaction of the “first-generation” Grubbs-type catalyst $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CH}_2$ (**1**) for the reaction with ethylene are studied. The most likely dissociative mechanism with trans olefin coordination is investigated for the metathesis reaction between the “first-” and the “second-generation” Grubbs-type catalysts **1** and $(\text{H}_2\text{IMes})(\text{PCy}_3)\text{Cl}_2\text{-Ru}=\text{CH}_2$ (**2**) with different substrates, ethylene, ethyl vinyl ether, and norbornene, and a profound influence of the substrate is found. In contrast to the degenerate reaction with ethylene, the reactions with ethyl vinyl ether and norbornene are strongly exergonic by 8–15 kcal/mol, and this excess energy is released after passing through the metallacyclobutane structure. While the metallacyclobutane is in a deep potential minimum for degenerate metathesis reactions, the energy barrier for the [2+2] cycloreversion vanishes for the most exergonic reactions. On the free energy surface under typical experimental conditions, the rate-limiting steps for the overall reactions are then either metallacyclobutane formation for **1** or phosphane ligand dissociation for **2**.

Introduction

Olefin metathesis is a powerful method for the formation of carbon–carbon double bonds.^{1–4} The elaboration⁵ and improvement of defined substrate and functional group tolerant ruthenium-based metathesis catalysts by Grubbs^{6–8} and others^{9–11} has broadened the scope of olefin metathesis significantly from bulk chemistry toward the synthesis of natural products and spurred the synthesis of even more varied structural variants as well as extensive mechanistic work. The activity of the “first-generation” ruthenium metathesis catalysts, of which **1(A)** is a representative, was significantly improved with the “second-generation” catalysts **2(A)**, where an *N*-heterocyclic carbene (NHC) replaces one phosphane group.^{6–10}

While the increased reactivity of “second-generation” catalysts was originally explained on the basis of an increased trans

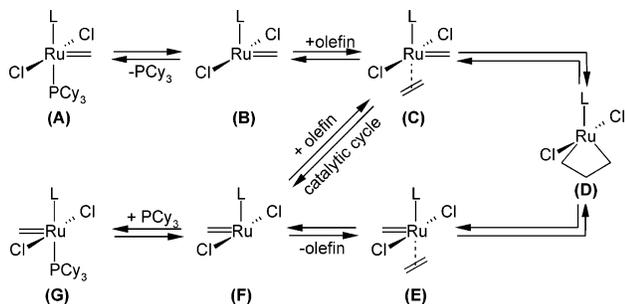
effect on the critical phosphane dissociation step⁴ that had been established, it was concluded from extensive in situ kinetic studies that the origin of the greatly increased activity derived from the increased reactivity of the four-coordinate 14-electron intermediate,^{12,13} which had already been observed as the active species for the “first-generation” systems in our gas-phase experiments.^{14,15} Recent comparative gas-phase experiments of the intrinsic reactivity of first- and second-generation catalysts **3** and **4** support Grubbs’ solution-phase studies.¹⁶

The principal steps of olefin metathesis involve according to the Chauvin mechanism¹⁷ a transition metal carbene which forms by coordination of an olefin a π complex. A formal [2+2] cycloaddition forms a metallacyclobutane. A [2+2] cycloreversion and dissociation finally leads to the olefin product (Scheme 1).

Although there is a general agreement for these principal steps, the detailed mechanism of olefin metathesis by ruthenium carbene complexes has been the subject of intense experimental^{12–28} and computational^{10,15,27–42} studies.

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Scheme 1. Most Likely Mechanism for Olefin Metathesis by Grubbs-type Ruthenium Carbene Complexes

The experimental studies are either performed in solution^{12,13,18,19,21–24,27,28} or in the gas phase^{14–16,24–26} by electro-spray ionization tandem mass spectrometry (ESI-MS/MS). Most of the computational studies consider only a few species of the catalytic cycle, focusing either on the ruthenium carbene formation process^{31–37} or on selected intermediates of the catalytic cycle,^{15,27,28,38} but there are also studies which treat the complete mechanism and eventually alternative reaction pathways.^{29,30,39–42} X-ray structures of complexes related to intermediates of the reactive cycle have also been determined,^{43–49}

related to possible intermediates of the postulated mechanisms for olefin metathesis by Grubbs-type ruthenium carbene complexes (Scheme 2).

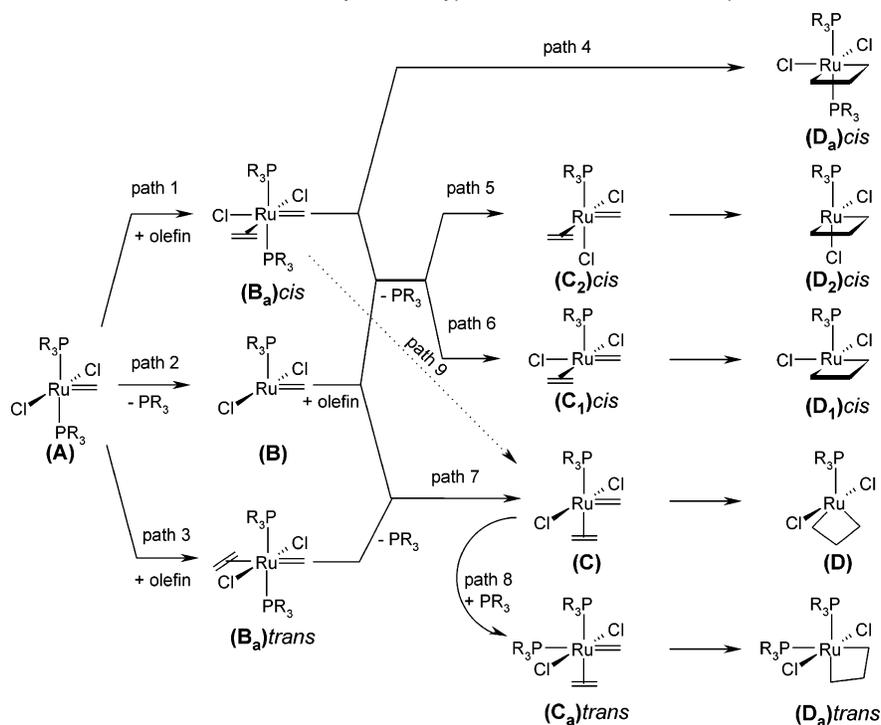
While there is currently a general agreement on the dissociative mechanism (Scheme 1), there is an ongoing discussion on the individual steps. They involve the nature of the metallacyclobutane which is considered as either an intermediate or a transition state,¹⁵ the configuration of the halides in the metallacyclobutane, cis or trans, and the rate-limiting step which can be either phosphane dissociation, metallacyclobutane formation, or cycloreversion. Computations have contributed a lot in clarifying the mechanism especially with respect to the structure of the involved intermediates. Yet most of these studies have investigated either model ligands or the model substrate ethylene. This does still leave room for interpretation concerning the steric and electronic influences of real ligands (PCy₃ and H₂Mes versus PH₃ and H₂IH) and substrates (ethyl vinyl ether and norbornene versus ethylene). Consequently, there is so far no unique explanation for the enhanced reactivity of the “second-generation” Grubbs-type ruthenium carbene complexes, and either different sterics,³⁸ a different topology of the hypersurface,⁴⁰ or a rate-limiting [2+2] cycloreversion versus a rate-limiting [2+2] cycloaddition³⁹ have been considered. Different substrates may add a further dimension of uncertainty to this question.

In fact, depending on the substrate, olefin metathesis can be divided into four classes: acyclic degenerate, acyclic exothermic, and ROMP with either an unstrained or a strained cyclic olefin as substrate. RCM and ADMET are covered by the acyclic degenerate and unstrained ROMP reaction. With respect to these four classes, four model substrates can be chosen: (a) ethylene (degenerate), (b) ethyl vinyl ether (acyclic exothermic), (c) cyclopentene (ROMP, unstrained), and (d) norbornene (ROMP, strained).

Experimentally, ethyl vinyl ether and norbornene are very important as substrates because almost all known catalysts react well with norbornene but only a few catalyze the olefin metathesis of linear olefins¹ and because olefin metathesis of vinyl ethers by first- and second-generation Grubbs initiators is irreversible.¹³ The reversibility of olefin metathesis with vinyl ethers has been reported for Cr,⁵⁰ W,^{51,52} and Re⁵³ carbene complexes. However, these substrates do raise new questions: because even within a small group of catalysts, notably first- and second-generation Grubbs-type catalysts, the behavior in acyclic metathesis toward electron-poor and electron-rich, branched and unbranched olefins is so different that it can be used as part of a synthetic strategy.⁵⁴ In ROMP, we have been able to show that the intramolecular bound π complex formed after opening of the metallacyclobutane with the living polymer chain is not only a resting state in ROMP, but its stability also affects overall rates in ROMP for different catalyst systems.^{14–16,24,25} Several resting states of the propagating

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Scheme 2. Postulated Mechanisms for Olefin Metathesis by Grubbs-type Ruthenium Carbene Complexes

polymer have recently been observed by Stelzer et al.⁵⁵ for ROMP of diester functionalized norbornene derivatives in solution. Furthermore, depending on the strain in the cyclic substrate, that is, cyclopentene and norbornene, the ROMP rate has been shown to be mainly affected by the rate of the back reaction, the ring-closing reaction, called “back-biting”, and not by the rate of the forward reaction.^{14,15}

For this study, we have computed the hypersurface for the reaction of **1(A)** and **2(A)** with ethylene, ethyl vinyl ether, and norbornene⁵⁶ [cyclopentene has already been treated on the QM/MM level in ref 56] as substrate including the whole ligand set.^{57–59} [The majority of the computational studies investigate a truncated model system (e.g., PH_3 instead of PCy_3). The size of the ligands (Tolman cone angles for PCy_3 and PH_3 are 170° and 87° , respectively, ref 57), their electronic properties, as well as their conformational flexibility, however, have a tremendous influence on catalyst stability – the 16-electron complex $(\text{PH}_3)_2\text{-Cl}_2\text{Ru}=\text{CH}_2$ has never been isolated nor detected – as well as on the catalytic reactivity (refs 23, 58, and 59). Treating the whole ligand system was indeed critical for the results of recent computational studies (refs 38 and 40).] We are trying to directly link the computational results to the corresponding experimental studies^{12,13,16} on these systems. We have also computed the energy surface for different model systems, where the PCy_3 and H_2IMes ligands have been replaced by PH_3 , PMe_3 , and H_2IH model ligands, to enhance comparability with former studies.^{15,39,41}

To create a firm basis for this study, all mechanisms, that have so far been discussed in the literature, are investigated for

the degenerate reaction of **1(A)** with ethylene as given in Scheme 2.

We claim that the given set of pathways investigated is complete in the sense that it covers every plausible reaction mechanism. Of course, this plausibility is especially difficult to prove for coordinatively labile transition metal complexes. Yet some restrictions concerning possible reaction pathways can be made without narrowing the scope of the study to narrow the set of problems.

(1) The mechanism has to be in agreement with the metallacyclobutane mechanism.¹⁷ The metallacyclobutane can be either a transition state or a minimum.

(2) The olefin has to be coordinated cis to the carbene before formation of the metallacyclobutane. This can be concluded from the fact that ring-closing metathesis works with small- to moderate-sized rings.¹⁸

(3) The principle of microscopic reversibility⁶⁰ has to be applicable, so the reaction mechanism has to be symmetric for a degenerate reaction.

(4) Free rotation of the carbene ligand and the coordinated olefin is assumed, and the phosphane ligand is considered to be perfectly symmetric with respect to the reaction coordinate. (More precisely, low barriers for conformational changes with respect to activation barriers for bond-forming/breaking steps in the catalytic cycle are assumed.)

(5) It is also desirable, but not necessary, to obtain a mechanism that can also be extended to Hofmann-type²⁷ and Hoveyda-type^{61–64} ruthenium carbenes.

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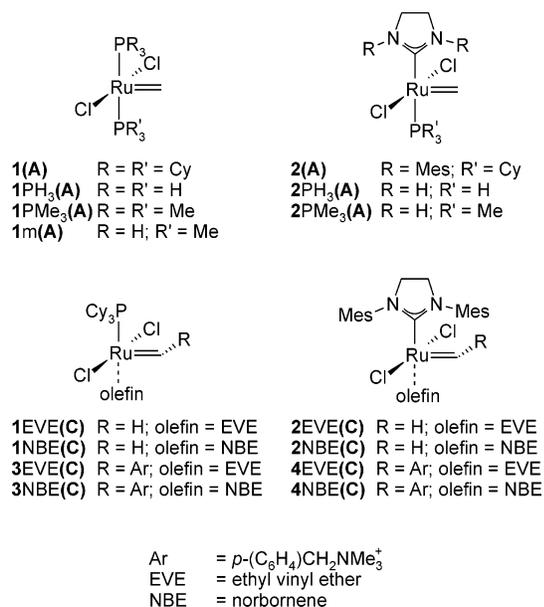


Figure 1. “First-generation” (**1,3**) and “second-generation” (**2,4**) Ru carbene complexes.

These mechanisms can be divided into two classes, into the associative mechanism where both phosphane ligands remain on the catalyst and into several dissociative mechanisms where the phosphane dissociates during catalysis either before or after coordination of the olefin. The dissociative mechanisms can be further divided into two subgroups, cis and trans according to the coordination of the olefin with respect to the phosphane.

For the sake of readability, a notation according to Figure 1 and Scheme 1 is used, where the first- and second-generation systems **1** and **2** are supplemented with a suffix **(A)**–**(G)** according to their position in the reactive cycle and **(TS)** for a transition state/structure. Model complexes obtain an additional suffix PH₃, PMe₃, and m for the mixed PH₃/PMe₃ system. The suffix EVE and NBE is added, when either ethyl vinyl ether or norbornene is used as substrate instead of ethylene.

Full-DFT calculations have been carried out with the ADF 2000.02 program, using the BP86 density functional^{65,66} which has already successfully been applied in former studies of olefin metathesis by Ru carbenes^{38–40} and reproduces the geometries well.⁴⁰ Computational details including optimized geometries and energies are given in the Supporting Information.

Results

Studying Alternative Mechanisms. Which One Fits Best?

(a) Associative Pathway. The associative pathway [there is no consistent notation in the literature; see for example refs 18 and 39] assumes that the olefin simply coordinates to the catalyst, forming an 18-electron olefin π complex, followed by the actual [2+2] cycloaddition and cycloreversion steps to form the product (Scheme 2, path 1/4).

Figure 2 shows the associative reaction of (PCy₃)₂(Cl)₂Ru=CH₂ (**1(A)**) with ethylene: Ethylene attacks **1(A)** along the bisector line of the Cl–Ru–C_{carbene} angle and thereby forces the chlorine into a cis conformation. The 18-electron olefin

complex **1(B_a)*cis*** is C_s symmetric. Formation of the metallacyclobutane proceeds via approach of the methylene and ethylene carbon atoms and synchronous rotation of the methylene group. While the transition state is C₁ symmetric, the metallacyclobutane product **1(D_a)*cis*** has C_s symmetry.

An alternative trans attack of the olefin to **1(A)** cannot lead to a productive metathesis cycle, because the olefin has to coordinate cis to the carbene for metallacyclobutane formation, as has already been concluded by Grubbs et al.,¹⁸ and the necessary rearrangement of a trans coordinated olefin complex into a cis coordinated complex within the octahedral coordination sphere is unlikely, although a cis to trans rearrangement is known for Ru(PPhMe₂)₂(Cl)₂(CO)₂,⁶⁷ which, however, may happen by dissociation/association rather than by a unimolecular step. As a consequence, there is only one associative pathway remaining, that is, path 1/4 in Scheme 2.

The relative DFT energies are $\Delta E = 0.0, >24.8, 5.5, >15.8$, and 11.3 kcal/mol for **1(A)**, TS **1(AB_a)*cis***, **1(B_a)*cis***, TS **1(BD_a)*cis***, and **1(D_a)*cis***, respectively. This is considerably lower than the 30.8 kcal/mol obtained by Fomine et al. for the coordination product of propene to **1(A)**.⁴¹ Yet the energies are in reasonable agreement with calculations on the PH₃ model system (PH₃)₂(Cl)₂Ru=CH₂ by Thiel et al.³⁹ (0.0, 12.8, 0.5, 4.4, and 0.7). Thiel et al. have also obtained a ~ 6 kcal/mol more favorable 18-electron olefin complex for the model system where the olefin is oriented \parallel to P–Ru–P. Although this is in analogy to a crystal structure of an isoelectronic Ru carbonyl olefin complex,⁴⁴ this conformation is sterically prohibitive for the real PCy₃ system. The steric strain imposed by the cyclohexyl rings in the PCy₃ system can be approximated to ~ 5 –15 kcal/mol by comparing the values for the PCy₃ system with those for the PH₃ system.³⁹

(b) Dissociative Pathways. The pathways 5–8 given in Scheme 2 are dissociative in the sense that there is at least one intermediate where one phosphane ligand is dissociated. Dissociation of the phosphane may occur either before (path 2) or after (paths 1 and 3) coordination of the olefin.

The olefin in the five-coordinate Ru olefin complex may be either in a cis (paths 5 and 6) or in a trans position (path 7) with respect to the phosphane. Consequently, the chlorine ligand in paths 5 and 6 has to stand cis with respect to each other. Paths 5 and 6 are distinguished from each other in the orientation of the chlorine ligands with respect to the phosphane, cis and trans in path 5 and all cis in path 6. Metallacyclobutane formation is then straightforward. A variant, where the phosphane again coordinates to the olefin complex (path 8), has recently been suggested.^{42,68} [Configurational fluxionality and isomerization processes at certain intermediate stages such as the isomerization of the cis dichloro metallacyclobutane into the trans dichloro isomer have been thoroughly investigated, and the activation barriers found are too high to play a significant role in the overall mechanism (ref 68). A detailed discussion on the ligand rotation of PCy₃ is given in ref 40.]

Figure 3 gives the structures and energies for the different possible dissociative pathways for the olefin metathesis reaction of ethylene by (PCy₃)₂(Cl)₂Ru=CH₂ (**1(A)**).

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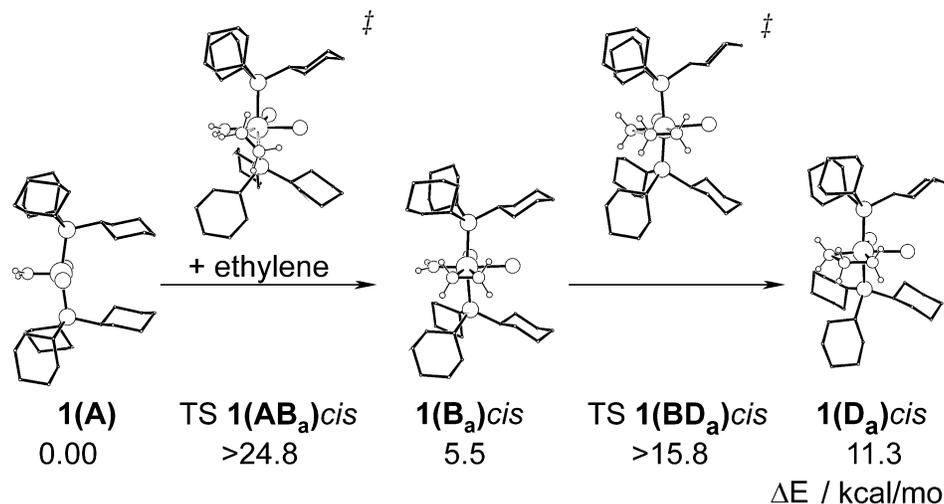


Figure 2. DFT energies ΔE and structures for the associative olefin metathesis of ethylene by **1** according to path 1/4 in Scheme 2. Transition states are marked with a “‡”.

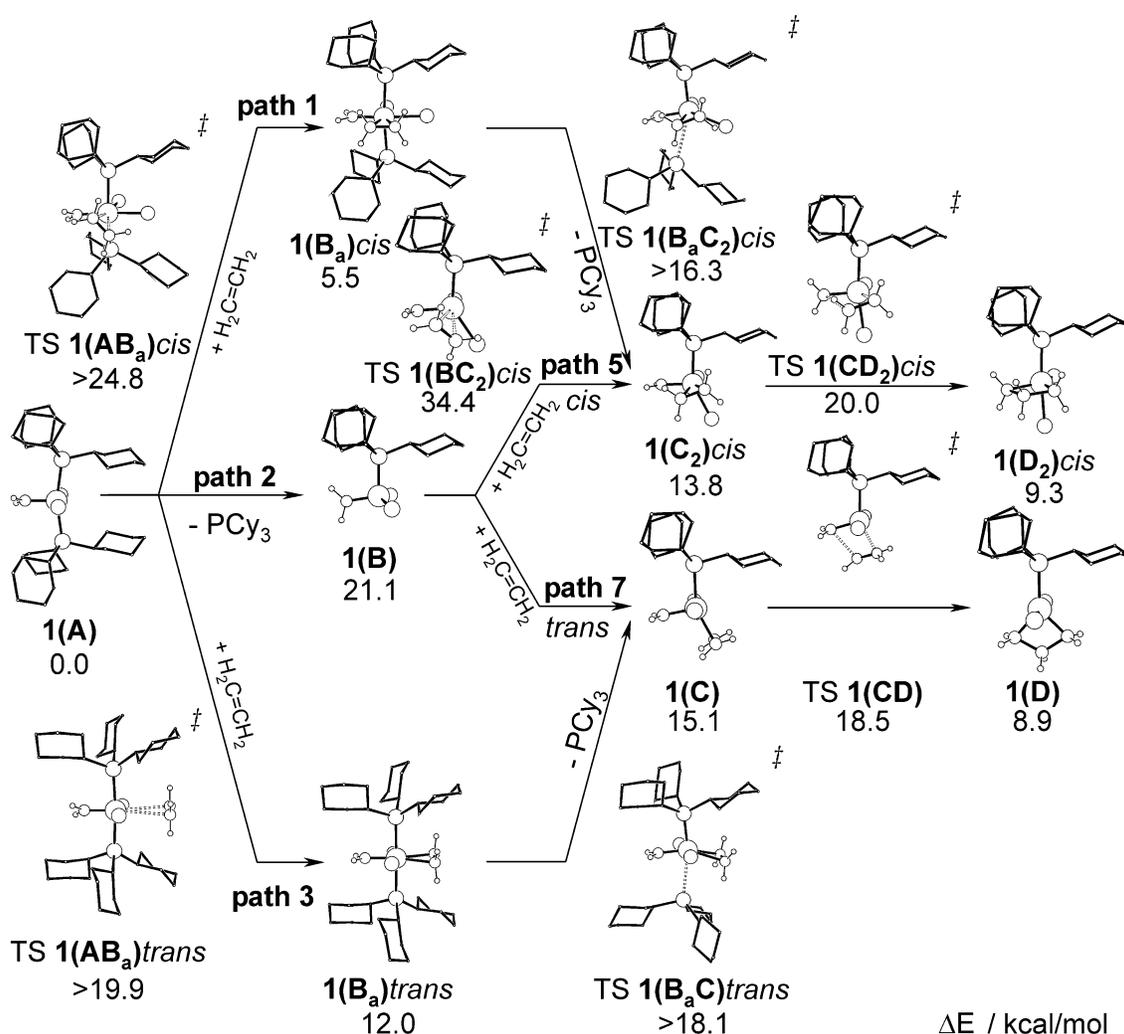


Figure 3. DFT energies ΔE and structures for a dissociative mechanism for the olefin metathesis of ethylene by **1** according to Scheme 2. Transition states are marked with a “‡”.

The simplest dissociative pathways start with the initial loss of a phosphane ligand (path 2), forming the 14-electron complex **1(B)** ($\Delta E = 21.1$ kcal/mol). The endothermic dissociation of PCy_3 proceeds without any enthalpic barrier beyond that due to ΔH of the reaction itself, although there may be an additional

contribution due to entropic effects. The sawhorse structure of **1(B)** is in agreement with the crystal structure of $(\text{PCy}_3)(\text{O}-t\text{-Bu})_2\text{Ru}=\text{CHPh}$.⁴⁵ The attack of the olefin on the 14-electron complex **1(B)** may occur either cis (path 5), along the bisector line of the $\text{Cl}-\text{Ru}-\text{C}_{\text{carbene}}$ angle, or trans (path 7) to the

phosphane ligand. Upon cis attack, the chlorine may be pushed either trans to the phosphane ligand (**1(C)₂cis**, path 5) or trans to the carbene (**1(C)₁cis**, path 6). Path 6 has originally been proposed on the basis of symmetry considerations but without experimental structural evidence for **1(C_a)cis**.¹⁸ Computationally, any attempt to find a minimum structure corresponding to **1(C₁)cis** has failed, and all starting structures have converged into **1(C₂)cis**. The structure for the 16-electron π complex **1(C₂)cis** is in agreement with the crystal structure of (H₂IMes)-(Cl)₂Ru[η^3 -(CHPh)(CPh)(CPh)]⁴⁹ that has been obtained during the olefin metathesis of (H₂IMes)(PCy₃)Cl₂Ru=CHPh with diphenyldiacetylene. Both steric and electronic reasons could account for the chloride's preference for the position trans to the phosphane. On one hand, a position cis to the sterically demanding PCy₃ ligand is avoided (the Tolman angle of PCy₃ is 170°),⁵⁷ and, on the other hand, a position trans to the carbene, which is a strong σ -donor, is avoided. As for the associative mechanism (path 1), a significant barrier for the coordination of the olefin of $\Delta E^\ddagger = 13.3$ kcal/mol (TS **1(BC₂)cis**) is a result of the necessary rearrangement of one chloride. Via TS (**CD₂**)_{cis}, the trigonal bipyramidal 14-electron metallacyclobutane (**D₂**)_{cis} is formed. The trigonal bipyramidal structure of (**D₂**)_{cis} is in contrast to the original assumption of a square pyramidal structure for the metallacyclobutane.^{18,19,49,69}

The critical points of the energy surface for the trans attack (path 7) of the olefin are $\Delta E = 15.1$, 18.5, and 9.0 kcal/mol for **1(C)**, TS **1(CD)**, and **1(D)**, respectively. Snapper et al.⁴⁷ have isolated an intramolecular trans dichloro ruthenium carbene olefin π complex during olefin metathesis of (PCy₃)₂Cl₂Ru=CHPh with a bicyclo[2.2.0]hexene derivative which matches excellently with **1(C)**. The structure of the metallacyclobutane **1(D)** is trigonal bipyramidal as in the case of (**D₂**)_{cis}, and the chlorines are on the axial position. While there is so far no crystal structure available for a ruthenium metallacyclobutane with the coordination number 5 (ruthenium metallacyclobutane complexes with the coordination number 6 are reported^{70,71}), Schrock et al.⁴⁸ have isolated the crystal of the isoelectronic five-coordinate 14-electron tungsten metallacyclobutane [OCMe-(CF₃)₂](*N*-2,6,-C₆H₃-*i*-Pr₂)W[CH(Me₃Si)CH(Me₃Si)CH₂- κ^2 C], which is trigonal pyramidal with the carbon atoms at the equatorial positions.

It may be mentioned here that the metallacyclobutane **1(D)** has no mirror plane or C₂ axis along the reaction coordinate. Therefore, to achieve a degenerate reaction, PCy₃ can either rotate by 180° ($\Delta E > 15.9$ kcal/mol, TS **1(DD')**) or the rotation can occur in a later reaction step at the cost of higher activation barriers for the subsequent steps, $\Delta E = 19.7$ and 16.6 for TS **1(DE)** and **1(E)**, respectively, as we have already reported on the basis of IMOMM calculations.⁴⁰

The most notable difference between paths 5 and 7 is the transition **1(B)** to **1(C)** which has no enthalpic barrier for the trans attack but an activation barrier of $\Delta E^\ddagger \approx 13.3$ kcal/mol for the cis attack, caused by the conformational change of one chlorine. The subsequent intermediates and transition states, the olefin π complex **1(B)**, the metallacyclobutane **1(D)**, and the

transition state **1(CD)**, are within 1.5 kcal/mol of the same energy for the cis as well as for the trans pathway.

An alternative route (and before our gas-phase investigations¹⁴ and the solution-phase NMR investigations by Grubbs et al.,^{12,13} also the favored one) into the dissociative mechanism has been the associative exchange of a phosphane by the olefin. [An associative exchange of the olefin substrate by a second olefin substrate at the level of (**C**) has also been investigated for **1(C)** and **2(C)** on the QM/MM level but was found to be not competitive (ref 68).] The olefin can attack either cis (path 1) or trans (path 3) to the carbene moiety and give two 18-electron intermediates which give upon loss of PCy₃ the same 16-electron olefin π intermediates as are found in the dissociative pathways 5 and 7, respectively. For the cis attack, path 1 is identical to the all-associative mechanism (Scheme 2, path 1/4 and Figure 2), and the energy ΔE for the transition state **1(B_aC₂)cis** is > 16.3 kcal/mol. The energies for the trans associative ligand exchange are $\Delta E = > 19.9$, 12.0, and > 18.1 for TS **1(AB_a)trans**, **1(B_a)trans**, and TS **1(B_aC)trans**, respectively. The highest transition state for the trans associative ligand exchange is ~ 5 kcal/mol lower in energy than that for the cis associative ligand exchange.

A variant of the trans dissociative mechanism has been suggested by Bottoni et al.⁴² They have postulated reassociation of the phosphane after formation of the olefin π complex (path 8, Scheme 2) and a C_{2v} symmetric octahedral six-coordinate ruthenium metallacyclobutane ($\Delta E = 4.0$ and 3.7 kcal/mol, relative to (**A**), for the PH₃ and PPh₃ model). The energies for the PH₃ model system are reproduced, but the energies for the C_{2v} symmetric intermediates **1(D_a)trans** with PCy₃ ligands are very high, with $\Delta E = 27.9$ and 30.2 kcal/mol. Moreover, these complexes adopt a square pyramidal structure with the metallacyclobutane in the apical position, where the σ -C atoms of the metallacyclobutane have approximated from 2.863 Å (PH₃ model) to 2.241 and 2.211 Å, which is already close to a cyclopropane formation.

Model Systems. In contrast to previous studies,^{15,29,30,39} the steric effects of the very large ligands (Tolman cone angles⁵⁷ for PCy₃, PMe₃, and PH₃ are 170°, 118°, and 87°, respectively) are explicitly treated. The full-DFT results for the real systems **1** and **2** (path 2/7) are compared to results obtained for model systems as have been used in earlier computational studies.^{15,29,30,39,41,42} It is important to note that only the real full-DFT system is able to reproduce the experimental results where the dissociation of PCy₃ is more feasible in the first-generation ruthenium catalyst despite their generally lower reactivity.^{12,13,22}

Figure 4 shows the DFT-optimized structures for the PH₃ and H₂IMes model systems **1PH₃(A)** and **2PH₃(A)**, as well as for the real PCy₃ and H₂IMes systems **1(A)** and **2(A)**. Besides modest changes in the bond distances going from the model system to the real system, notably the conformation of the ligands changes. As a consequence of reduced steric demand in the model systems **1PH₃(A)**, **2PH₃(A)**, **1PH₃(C)**, and **2PH₃(C)**, the methylene can for instance adopt the electronically preferred staggered conformation with respect to the chlorides.

However, the most notable difference between model systems and real systems is the orientation of the NHC ligand. In **2PH₃**, the plane of the H₂IMes ligand is eclipsed with respect to the chlorides, whereas in **2** the imidazolidinylidene plane is staggered. This is the result of steric interactions between the mesityl

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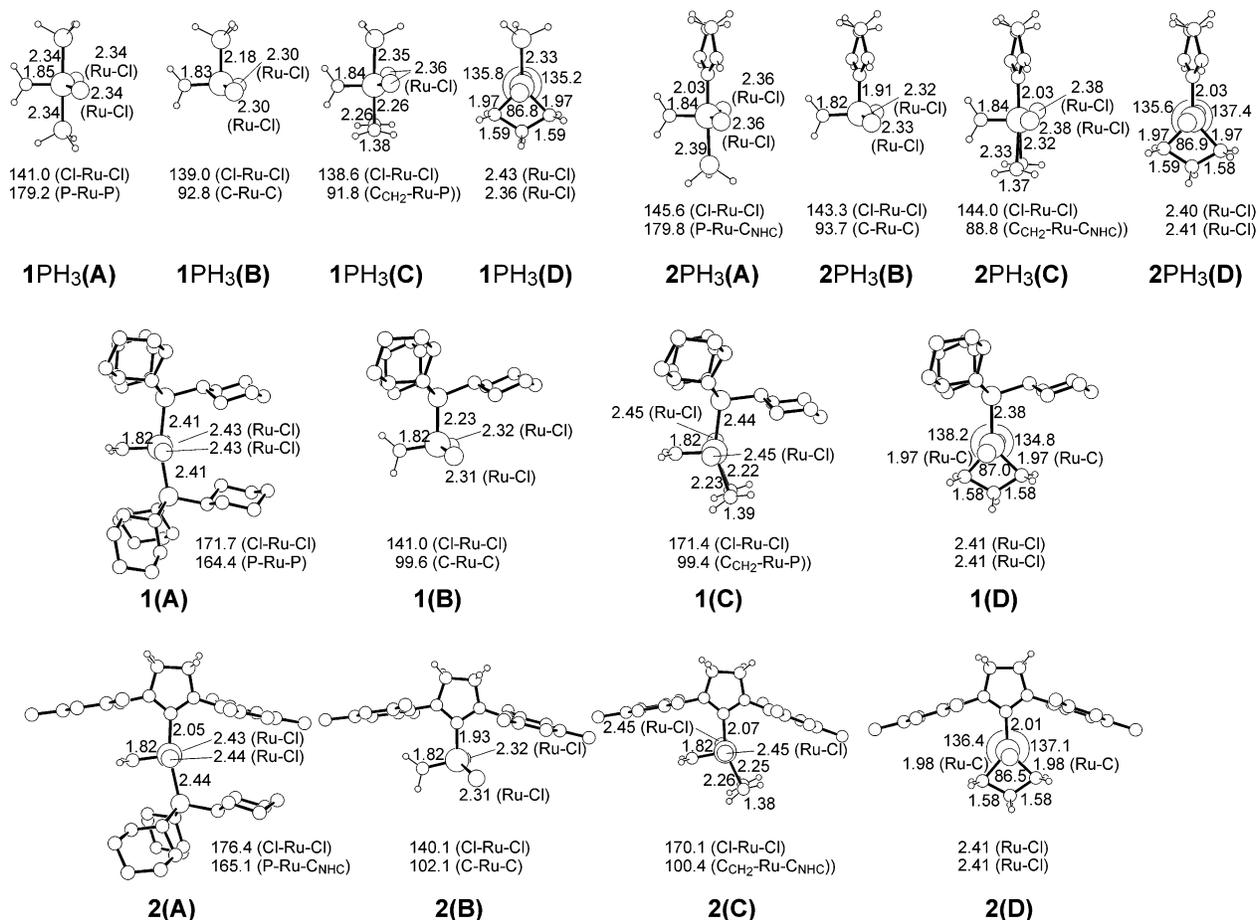


Figure 4. Full-DFT-optimized structures of important intermediates for the olefin metathesis reaction by first- and second-generation ruthenium carbene catalysts for the PH₃ and H₂IH model systems 1PH₃ and 2PH₃ and the real PCy₃ and H₃IMes systems 1 and 2.

residues and the chloride ligands. Given the conclusion by Cavallo³⁸ where the steric interaction between the mesityl and the methylene in **2(B)** is assumed to be one of the driving forces for the faster olefin metathesis by second-generation ruthenium carbene catalysts, the inclusion of the mesityl residues into the calculations is essential.

The energies for different model systems are given in Table 1. The dissociation energies for PCy₃, computed for the real systems with $\Delta E = 21.1$ and 26.1 kcal/mol, agree well with the experimental values for the corresponding benzylidene complexes, $\Delta H = 23.6 \pm 0.5$ and 27 ± 2 kcal/mol.¹³ The contribution of relaxation energies of the PR₃ ligand is too small to account for different PR₃ dissociation energies. Interestingly, in 1PH₃, the PH₃ dissociation energy of $\Delta E = 21.5$ kcal/mol is in good agreement with the dissociation energy for PCy₃ in the real system. It seems that the stronger π acidity^{72,73} and the weaker basicity of PH₃ as compared to those of PCy₃ are compensating for each other. The strong sensitivity of ligand dissociation energies on π acidity and σ basicity and a dramatic trans effect are observed in the dissociation energies of the mixed complex (PMe₃)(PH₃)(Cl)₂Ru=CH₂. The dissociation energies differ by $\Delta\Delta E = 15.6$ kcal/mol. In the second-generation systems, dissociation of the phosphane ligands is more feasible than dissociation of the NHC ligand, which is

Table 1. ΔE Values for Different Model Systems of Important Intermediates for the Olefin Metathesis Reaction by First- and Second-Generation Ruthenium Carbene Catalysts^a

system	ΔE				
	1, 2	1PMe ₃ , 2PMe ₃	1PH ₃ , 2PH ₃	1m, 2	1m, 2PH ₃
remaining ligand	PCy ₃	PMe ₃	PH ₃	PH ₃	PMe ₃
dissociating ligand	PCy ₃	PMe ₃	PH ₃	PMe ₃	PH ₃
(A)	0.0	0.0	0.0	0.0	0.0
(B)	21.1	28.3	21.5	32.8	17.2
(C)	15.1	16.6	6.7	18.0	5.5
TS (CD)	18.5	29.1	21.5	31.5	18.0
(D)	8.9	20.2	14.3	25.6	9.2
$\Delta E_{\text{relax}}(\text{PR}_3)^b$	-3.6	-1.7	-1.7		
remaining ligand	H ₂ IMes	H ₂ IH	H ₂ IH	PCy ₃	PH ₃
dissociating ligand	PCy ₃	PMe ₃	PH ₃	H ₂ IMes	H ₂ IH
(A)	0.0	0.0	0.0	0.0	0.0
(B)	26.1	27.6	18.4	38.1	52.3
(C)	15.0	14.5	5.2	32.1	37.5
TS (CD)	17.3	25.6	16.3	35.4	52.3
(D)	5.3	15.9	6.7	26.0	45.1
$\Delta E_{\text{relax}}(\text{PR}_3)^b$	-3.8	-1.4	-1.0		

^a Relative energies are given in kcal/mol with starting structures (A) as reference at zero energy and are mass balanced for PH₃ (PMe₃) and ethylene, respectively. ^b Relaxation energies for PR₃ upon dissociation from (A).

consistent with the hypothesis that in these systems the phosphane rather than the NHC ligand is lost during olefin metathesis,^{7,9,10,74,75} and the dissociation energy for PR₃ of the real system **2(A)** and the model system **2PH₃(A)** differs by 8.9 kcal/mol.

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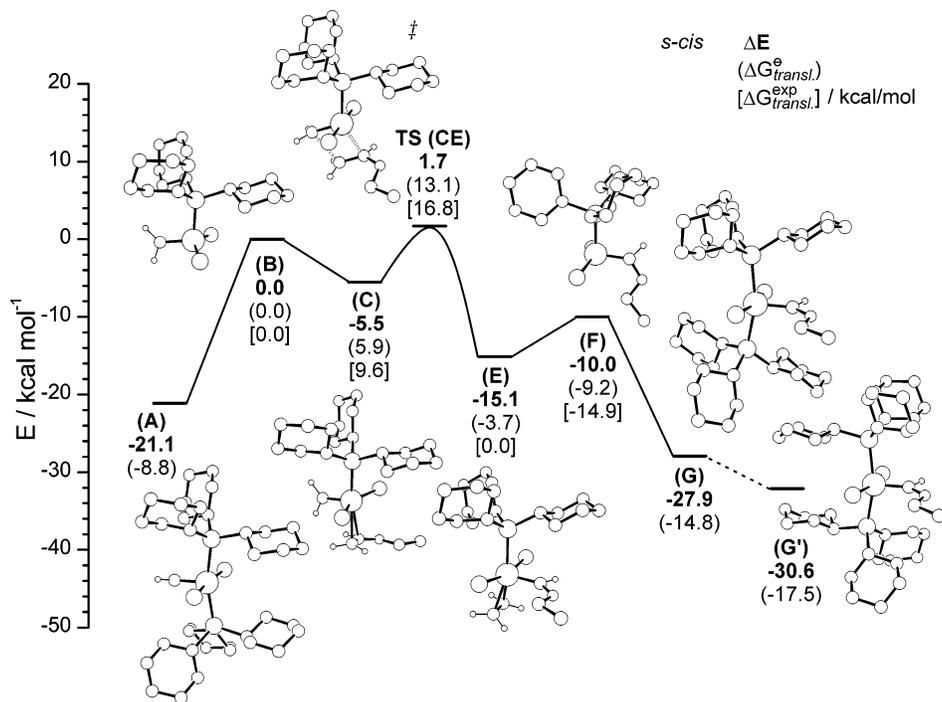


Figure 5. Structures and mass balanced relative energies ΔE for the reaction of **1(A)** with ethyl vinyl ether given in kcal/mol. The complex **1(B)** is taken as the reference structure at zero energy. Free energies $\Delta G_{\text{transl}}^0$ and $\Delta G_{\text{transl}}^{\text{exp}}$ are comprised only of the translational entropy contribution. Experimental conditions for $\Delta G_{\text{transl}}^{\text{exp}} = 8.45$ mTorr, $T = 343$ K, $[\text{Ru}]:\text{EVE} = 1:5000$. Hydrogens on the ligand are omitted for clarity.

The increasing olefin affinity for the PCy_3 , PMe_3 , and PH_3 complexes ($\Delta\Delta E_{(\text{BC})}$) is consistent with a reduced basicity and an increased π acidity in the order PCy_3 , PMe_3 , and PH_3 and the assumption that electron-withdrawing groups destabilize the 14-electron complex (**B**) more than the 16-electron complex (**C**).

The relative stability of the 14-electron metallacyclobutanes (**D**) as compared to that of (**B**) shows an exactly opposite trend with $\Delta\Delta E = -12.2$, -8.1 , and -7.2 kcal/mol. Here, the electron-withdrawing properties of the ligand destabilize the 14-electron metallacyclobutane species relative to the 14-electron carbene species (**B**), because electron deficiency in the 14-electron carbene complexes (**B**) is partly compensated by conjugation with the carbene, whereas in the metallacyclobutane conjugation and thus compensation for electron deficiency are interrupted.

The stabilization of the metallacyclobutane intermediate is even more profound in carbene complexes with NHC ligands, as the NHC ligands are very strong σ donors⁷⁶ but only weak π acids.^{72,73}

Changing the Substrate. Although a tremendous influence of the substrate on olefin metathesis is found experimentally, this has not yet been subject to theoretical investigations.

Usually, either the computations have been carried out with ethylene as a substrate,^{15,38,39,42} starting with the methylene^{15,39,42} or benzylidene³⁸ complex, or they have used propene⁴¹ as substrate starting with the methylene complex. In our own calculations,⁴⁰ the benzylidene complex has been reacted with styrene. The sole examples where the role of the substrate has been considered are studies by Cavallo³⁸ and Coalter et al.^{31,32} Cavallo has theoretically investigated our gas-phase experiments

with 1-butene and norbornene^{14,15} for the PH_3 benzylidene complex, focusing on the debate of whether the metallacyclobutane was an intermediate or a transition state. Coalter et al. have also investigated the different behavior of ethylene and vinyl ethers in the proposed formation of ruthenium carbene complexes starting with $(P\text{-}i\text{-Pr}_3)_2\text{ClRuH}$ and olefin. Here, we are in particular interested in the exergonic reaction of first- and second-generation Grubbs-type catalysts with ethyl vinyl ether and norbornene, as these substrates have been subject to many mechanistic experimental studies.

(a) Reaction with Ethyl Vinyl Ether. Figure 5 gives the structures and energies for the reaction of $(\text{PCy}_3)_2(\text{Cl})_2\text{Ru}=\text{CH}_2$ (**1(A)**) with ethyl vinyl ether. [The preference of the *s-cis* over the *s-trans* conformers is in general small and $\Delta E_{\text{IMOMM}} = 0.5$ kcal/mol for TS **1EVE(CE)** and even inverse on the ΔE_{DFT} -surface (-1.0 kcal/mol). Only intermediate **1EVE(F)** shows a strong preference for the *s-cis* over the *s-trans* conformer.] The most notable difference in the ΔE -surface as compared to the reaction with ethylene is the absence of the metallacyclobutane intermediate **1EVE(D)**, which is in a 3.4 kcal/mol deep minimum for the reaction with ethylene. However, a thorough investigation around the hypothetical structure of the metallacyclobutane reveals a flattening of the potential around the typical C–C bond distance for the metallacyclobutane ($\Delta E = 0.23$ kcal/mol between 1.69 and 1.79 Å for $\text{C}_{(\text{H}_2)}-\text{C}_{(\text{HOEt})}$). Interestingly, for the *s-trans* conformer, a metallacyclobutane intermediate has been found at $\Delta E_{\text{IMOMM}} = -13.6$ kcal/mol. It has, however, a very small activation barrier for the ring-opening process, $\Delta E_{\text{IMOMM}}^\ddagger = 0.8$, which vanishes by adding the zero-point energy corrections (typically 0.6–0.9 kcal/mol, see Table 2). Its $\text{C}_{(\text{H}_2)}-\text{C}_{(\text{HOEt})}$ bond distance of 1.660 Å is very long, whereas the $\text{C}_{(\text{H}_2)}-\text{C}_{(\text{H}_2)}$ bond is shortened to 1.534 Å. The corresponding bond distances for the reaction with ethylene are 1.580 and 1.587 Å. [The question of whether the ethyl vinyl

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Table 2. Relative Energies, ΔE , Zero-Point Energy Corrected Relative Energies, ΔE_{ZPE} , Relative Enthalpies and Relative Free Energies at Standard Conditions, ΔH° and ΔG° , and Relative Translational-Only Free Energies ΔG_{transl} at Standard Conditions Are Given in kcal/mol with Starting Structures (**A**) as Reference at Zero Energy and Are Mass Balanced for PH_3 (PMe_3) and Ethylene, Respectively

	ΔE	ΔE_{ZPE}	ΔH°	ΔG°	ΔG_{transl}
1 PH_3 (A)	0.0	0.0	0.0	0.0	0.0
1 PH_3 (B)	21.5	19.3	19.0	8.2	10.7
1 PH_3 (C)	6.7	6.2	6.4	8.0	6.5
TS 1 PH_3 (CD)	21.5	20.2	20.3	21.7	21.3
1 PH_3 (D)	14.3	14.8	14.2	17.1	14.1
1 PMe_3 (A)	0.0	0.0	0.0	0.0	0.0
1 PMe_3 (B)	28.3	27.1	26.7	12.8	16.9
1 PMe_3 (C)	16.6	17.2	17.3	16.1	15.8
TS 1 PMe_3 (CD)	29.1	29.0	28.9	27.6	28.3
1 PMe_3 (D)	20.2	22.2	21.9	21.1	19.5
2 PH_3 (A)	0.0	0.0	0.0	0.0	0.0
2 PH_3 (B)	18.4	16.1	15.9	4.5	7.6
2 PH_3 (C)	5.2	4.8	5.0	6.6	5.1
TS 2 PH_3 (CD)	16.3	15.2	15.0	17.1	16.1
2 PH_3 (D)	6.7	7.5	7.3	9.0	6.5

ether adduct is η^2 - π bound or κ^1 - O bound was important for the interpretation of our gas-phase experiments, where we have concluded from comparative collision experiments with diethyl ether that π coordination is dominant (ref 24). Computationally, the distinction can be made with ethyl vinyl ether itself, and the κ^1 - O adduct is found to be 2.3 kcal/mol less stable than the π adduct **1EVE(C)**. An alternative η^3 - π coordination has not been considered yet.]

Comparison of the starting complex **1(A)** to its product **1EVE(G')** reveals that the overall reaction with ethyl vinyl ether is ~ -9.5 kcal/mol exothermic. However, it is more appropriate to compare **1(B)** to its ethoxy carbene analogue **1EVE(B)**, because they have an identical conformation of the cyclohexyl rings and therefore additional interactions between the ethoxy group and the cyclohexyl rings are avoided. Their difference in energy is $\Delta E = -10.0$ kcal/mol.

The energy of the transition state for the reaction with ethyl vinyl ether, TS **1EVE(CE)** with $\Delta E^\ddagger = 7.1$ kcal/mol, is higher than the energy of the transition state for metallacyclobutane formation with ethylene, TS **1EVE(CE)**, which is $\Delta E^\ddagger = 3.4$ kcal/mol (Figure 3). In fact, it is even the highest point in the ΔE -surface, 1.7 kcal/mol higher than the 14-electron complex **1(B)**.

Structures and energies for the reaction of $(\text{H}_2\text{IMes})(\text{PCy}_3)_2(\text{Cl}_2)\text{Ru}=\text{CH}_2$ (**2**) with ethyl vinyl ether are given in Figure 6. The ΔE -surface for **2** is analogous to that of the surface of **1**. The energies for the *s-cis* and the *s-trans* conformers are again comparable with a small preference for the *s-cis* conformers, and the reaction for the second-generation catalyst is again very exothermic with $\Delta E = -13.6$ kcal/mol for $\Delta E_{2(\text{B})} - \Delta E_{2\text{EVE}(\text{F})}$ and -8.0 kcal/mol for $\Delta E_{2(\text{A})} - \Delta E_{2\text{EVE}(\text{G}')}$.

Notable differences to the first-generation catalyst **2** are, on one hand, the presence of a minimum for the metallacyclobutane in the *s-cis* conformer at $\Delta E = 11.3$ kcal/mol, which is consistent with the fact that in the case of the reaction with ethylene, the second-generation metallacyclobutane **2(D)** is more stable than the first-generation metallacyclobutane **1(D)**. This minimum, however, is smaller than the zero-point energy. On the other hand, the transition state for the metallacyclobutane

formation of TS **2EVE(CD)** is lower than that for the first-generation catalyst and 5.0 kcal/mol below the energy of the 14-electron complex **2(B)**.

(b) Reaction with Norbornene. It is very fruitful to compare the energy surface for olefin metathesis of norbornene by **1** (Figure 7) with that of ethylene, Figure 3, path 2/7. Dissociation of PCy_3 and formation of the 14-electron species **1(B)** are identical. The first difference concerns the coordination of the olefin and formation of the π complex **1(C)**. Norbornene can coordinate either exo parallel to the methylene group or exo perpendicular. In addition, the methylene group can adopt different rotational conformations, but the energy differences are small. Upon perpendicular coordination, the methylene bridge in norbornene can either be in an anti or in a syn orientation with respect to the carbene. The energies are $\Delta E = -6.9$ (ll), -7.4 (\perp -anti), and -5.2 kcal/mol (\perp -syn). The norbornene π complex is stronger than the ethylene π complex ($\Delta\Delta E = 1.4$ kcal/mol), although norbornene is sterically more demanding. This preference can be attributed to the pyramidalization of the olefinic unit in norbornene, which makes it a better donor.

The lowest transition state for metallacyclobutane formation, starts, different from the reaction with ethylene, with the ll coordinated π complex and not with the \perp -anti conformer that is lower in energy. The reason is a higher rotational barrier of the π coordinated norbornene around the coordination axis due to steric interactions between the methylene bridge of norbornene and the chlorine atoms.

Metallacyclobutane formation of TS **1NBE(CD)** is more difficult for norbornene than for ethylene, $\Delta E^\ddagger = 5.9$ and 3.4 kcal/mol, which is in agreement with the results for the PH_3 model system by Cavallo.³⁸ The C–C bond distance of the newly formed bond is 2.348 Å at the transition state, TS **1NBE(CD)**.

The energy of the metallacyclobutane **1NBE(D)** is close to the energy of the ethylene analogue **1(D)** ($\Delta E = -12.9$ and -12.2 kcal/mol), and the C–C bond lengths of $\text{C}_{(\text{H}_2)}-\text{C}_{(\text{HR})} = 1.551$ Å and $\text{C}_{(\text{HR})}-\text{C}_{(\text{HR})} = 1.645$ Å are less asymmetric than in the case of ethyl vinyl ether (NHC system). This indicates that the strain energy of ~ 15 kcal/mol^{40,77} present in norbornene has not yet been released in the metallacyclobutane, as has already been argued in the interpretation of the experimental data.¹⁵

It is upon opening of the metallacyclobutane that the strain energy in norbornene is partly released, and, according to Hammond's postulate,^{78–80} the transition state is with $\text{C}_{(\text{HR})}-\text{C}_{(\text{HR})} = 2.032$ Å considerably more metallacyclobutane-like than the transition state TS **1NBE(CD)** with $\text{C}_{(\text{H}_2)}-\text{C}_{(\text{HR})} = 2.348$ Å. The activation barrier for the ring opening of the metallacyclobutane is reduced to 2.1 kcal/mol.

The product of the [2+2] cycloreversion, **1NBE(E)**, is an intramolecularly bound π complex that has already been postulated in our gas-phase studies.^{14,25} The energy difference between intermediates **1NBE(C)** and **1NBE(E)** of $\Delta\Delta E = 12.2$ kcal/mol indicates that most of the strain energy of norbornene (~ 15 kcal/mol)^{40,77} is now released.

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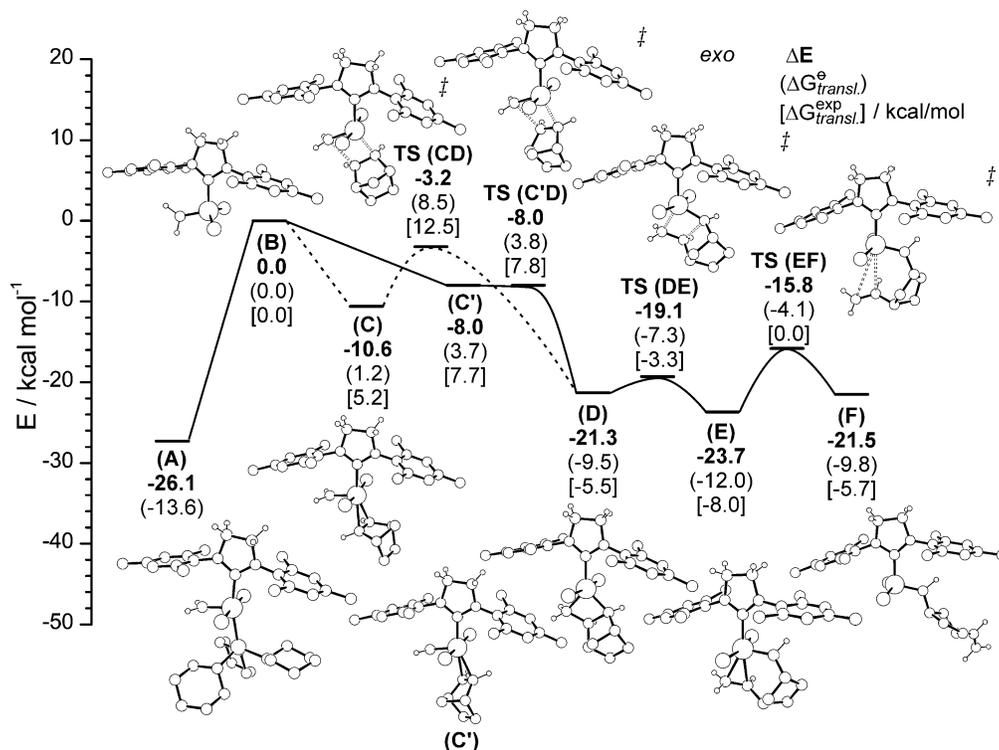


Figure 8. Structures and mass balanced relative energies ΔE for the reaction of **2(A)** with norbornene given in kcal/mol. The reactant complex **2(A)** is taken as the reference structure at zero energy. Free energies $\Delta G_{\text{transl}}^{\circ}$ and $\Delta G_{\text{transl}}^{\text{exp}}$ are comprised only of the translational entropy contribution. Experimental conditions for $\Delta G_{\text{transl}}^{\text{exp}} = 8.45$ mTorr, $T = 343$ K, $[\text{Ru}]:\text{EVE} = 1:5000$. Hydrogens on the ligand are omitted for clarity.

the imidazole ring lies in the $C_{\text{carbene}}\text{-Ru-C}_{1,\text{imidazole}}$ plane, whereas in the IMOMM-optimized structures, the NHC ligand adopts C_2 symmetry and twists by $\sim 15\text{--}20^\circ$ with respect to the $C_{\text{carbene}}\text{-Ru-C}_{1,\text{imidazole}}$ plane (ref 68).]

Similar to the reaction with ethyl vinyl ether, there are only small differences between the energy surface of first- and second-generation catalysts $(\text{PCy}_3)_2(\text{Cl})_2\text{Ru}=\text{CH}_2$ (**1**) and $(\text{H}_2\text{-IMes})(\text{PCy}_3)(\text{Cl})_2\text{Ru}=\text{CH}_2$ (**2**). The major difference is the relative stability between the 14-electron metallacyclobutane and the 16-electron π complex, $\Delta E_{\text{nNBE(C)}} - \Delta E_{\text{nNBE(D)}} = -5.5$ kcal/mol for **1**/ \perp , -5.9 for **1**/ \parallel , -10.7 for **2**/ \perp , and -13.2 for **2**/ \parallel .

As a consequence, the transition states leading to the metallacyclobutane are lower, the barrier starting from the parallel π complex **2NBE(C')** is only $\Delta E^\ddagger = 0.1$ kcal/mol, and the transition state is more similar to the reactant as indicated by a longer C–C distance (2.377 Å) than for **1NBE(C)**. The activation barrier for the reaction starting with the \perp -anti π complex **2NBE(C)** requires a sterically hampered rotation of norbornene and is therefore significantly higher, with $\Delta E^\ddagger = 7.3$ kcal/mol and a C–C bond length of 2.343 Å.

The barrier for ring opening of the metallacyclobutane **2NBE(DE)** is as low as that for the PCy_3 system **1**, with $\Delta E^\ddagger = 2.2$ kcal/mol, and the transition state is close to that of the metallacyclobutane ($C_{\text{HR}}\text{-}C_{\text{HR}} = 2.029$ Å).

Again, the intramolecular π complex **2NBE(F)** is in a deep energetic minimum (it is even the lowest structure in the metathesis cycle after formation of the 14-electron complex **2(B)**), and the activation barrier for the regeneration of the active 14-electron species with $\Delta E^\ddagger = 7.9$ kcal/mol is even higher than that for the first-generation catalyst. The distance of the olefin from the metal ($\text{Ru-center}_{(\text{H}_2\text{C}=\text{CHR})}$) is 3.694 Å at the transition state. An important difference between **1** and **2** is the

relative stability of **NBE(E)** and **NBE(F)**. They have approximately the same stability in the first-generation system, $\Delta\Delta E = 0.6$ kcal/mol, whereas in the second-generation systems the intramolecular π complex is favored by $\Delta\Delta E = 2.3$ kcal/mol.

Discussion

The Most Favorable Pathway. The energy surface of different pathways for metallacyclobutane formation, the half-way point of olefin metathesis, by the Grubbs-type ruthenium carbene complex **1(A)** has been calculated, including the full PCy_3 ligand. The set of studied pathways is considered to be complete within the Chauvin mechanism.¹⁷ Whether one reaction pathway is favored as compared to an alternative pathway does not depend on relative energy differences of individual steps but on the absolute energy of the highest transition state (intermediate).

According to their activation energies ΔE^\ddagger , two reaction pathways become favorable. The first is the dissociative pathway initiated by the formation of the 14-electron complex **1(B)** (path 2, Scheme 2) with subsequent coordination of the olefin trans to the phosphane ligand **1(C)**. Dissociation of the phosphane and association of the olefin are both free of activation enthalpy because they proceed without considerable rearrangement of the complex. Metallacyclobutane formation (path 7) leads to the trigonal bipyramidal metallacyclobutane intermediate **1(D)**. A second possibility is pathway 3, where olefin metathesis is initiated by a trans associative exchange of the phosphane ligand by the olefin. The subsequent metallacyclobutane formation is equivalent to that in path 2/7.⁸¹ [A distinction based on crystal structures reveals that all intermediates in the postulated dissociative pathway (path 2/7) have representative crystal

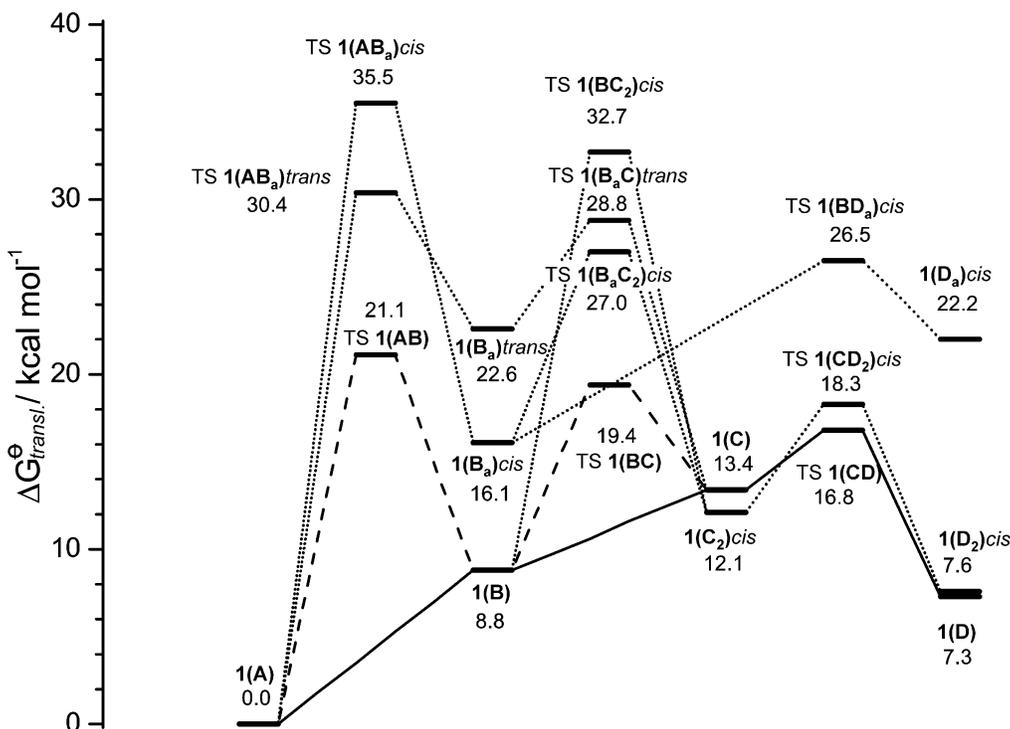


Figure 9. $\Delta G_{\text{transl}}^{\circ}$ -surface for olefin metathesis of ethylene by **1(A)**. Free energies are given in kcal/mol. Different pathways corresponding to Figures 2 and 3 are shown. The solid line shows the most favorable pathway 2/7. The dotted lines show less favorable alternative pathways. The dashed line is the upper $\Delta G_{\text{transl}}^{\circ}$ -limit for loss of PCy_3 (TS **1(AB)**) and coordination of ethylene (TS **1(BC)**).

structure analogues (structures in refs 45, 47, and 48 for **1(B)**, **1(C)**, and **1(D)**). There is no analogue crystal structure for intermediate **1(B_a)_{trans}** in path 3. The isoelectronic cis isomer of a ruthenium olefin carbonyl complex, however, exists. This preference for the cis complex is also reflected in the relative energies of **1(B_a)_{cis}** and **1(B_a)_{trans}**, where **1(B_a)_{cis}** is 6.50 kcal/mol lower in energy than **1(B_a)_{trans}**. Photochemical and thermal isomerization of the cis and trans ruthenium dicarbonyl precursor for the olefin carbonyl complex has been reported.⁶⁷ While the crystal structures confirm that the computed structures are reasonable and may also exist in reality, a distinction between either of the two pathways cannot be made on the basis of available crystal structures alone, because as has been elegantly demonstrated by Halpern,⁸¹ the most abundant (and therefore crystallizing) complex in solution need not be a part of the most favorable catalytic cycle; it may represent, in fact, a dead end. Interestingly, in the first detailed solution-phase mechanistic investigation, Grubbs et al. (ref 18) have found that the all-associative path could only contribute less than 5% to the catalyst turnover. However, they have not considered the formation of the 14-electron species **B**, but only an all-associative path 1/4 and an associative/dissociative path 1/6.]

Rather than on the ΔE -surface, the distinction between paths 2/7 and 3 would need to be made on the ΔG -surface where dissociative steps are favored by ~ 12 kcal/mol as has been shown by Thiel et al.³⁹ on the model systems. This, however, brings in the computationally prohibitive statistical mechanical treatment of the real systems. Yet the major entropy contribution in the catalytic cycle for olefin metathesis arises from the loss and gain of translational entropy by changing the number of involved particles. This assumption is in particular true for our

gas-phase experiments,^{14–16} where we do not have to account for solvation entropy.

In statistical gas theory, a relation between entropy and the number of particles is given by the Sackur–Tetrode equation.⁸² In our case, the translational entropy in paths 2 and 3 ranges from 36 to 45 cal mol⁻¹ K⁻¹ or from -11 to -14 kcal/mol at 298 K for each additional molecule. Table 2 gives both the relative free energies ΔG° obtained from second-order derivatives and the approximated relative free energies $\Delta G_{\text{transl}}^{\circ}$ where only the translational entropy contribution is considered. As can be seen for the model systems, this approximation is within 4 kcal/mol correct.

Figure 9 gives the $\Delta G_{\text{transl}}^{\circ}$ profile of different pathways for olefin metathesis of ethylene by **1** according to Figures 2 and 3. On the $\Delta G_{\text{transl}}^{\circ}$ -surface, the dissociative pathway 2/7 is favored by 13.6 kcal/mol. Thiel et al.³⁹ have also found a clear preference for the dissociative pathway 2/7 on their ΔG° -surface for the model compounds. In solution, this entropic contribution is expected to be reduced by the solvation entropy of the dissociated particles, but this contribution is expected to be small, as $\Delta S_{\text{solv}}^{\circ}$ for H^+ in water is, for example, ~ -1.2 cal K⁻¹ mol⁻¹.

As has already been mentioned, there is no enthalpic (or ΔE) barrier for the coordination of ethylene to **1(B)**. For the free energy of activation, an upper limit of 10.6 kcal/mol is given by the assumption that at the transition state TS **1(BC)** the two fragments, the 14-electron complex **1(B)** and ethylene, have already lost their individual degrees of translational motion before feeling any attractive potentials such as dipole–dipole or van der Waals interactions. The same consideration for the

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association of PCy_3 to **1(B)** gives an upper limit for the free energies of activation $\Delta G_{\text{transl}}^\ddagger$ of 12.3 kcal/mol (TS **1(BA)**). Interestingly, Grubbs et al. have found activation entropies of $\sim 12 \text{ cal mol}^{-1} \text{ K}^{-1}$ ($\sim 3.5 \text{ kcal/mol}$) for the reaction **(A)** \rightarrow **(B)** in solution,¹³ which is one-third of the estimated upper limit.

Although the qualitative picture for the mechanism of olefin metathesis has not changed by studying the real complex **1(A)** rather than the model systems,³⁹ the results presented here can serve as a quantitative basis: For the all-associative mechanism, the 18-electron PCy_3 species are by ~ 5 to 15 kcal/mol increased in energy as compared to the PH_3 models.³⁹ [Path 7 has not been covered by Thiel et al., but one can estimate from the analogy with the computed structures that it will be at least ~ 5 kcal/mol higher in energy for the PCy_3 system than for the PH_3 model system.] However, the critical points for the dissociative pathway, where only coordinative unsaturated complexes are involved, only differ by ~ -3 to 9 kcal/mol.³⁹

Although the PCy_3 methylene complex **1** exists and olefin metathesis with ethylene is known (ethylene is the product in ADMET and the methylene complex is an intermediate in ADMET and most of the RCM reactions; see for example ref 22), it is still more a kind of model system than a real system. First, in ROMP and RCM, mostly the benzylidene complex rather than the methylene complex **1** is used as a precatalyst, and, second, the substrates are usually larger than ethylene. This may impose additional steric problems: In the dissociative pathway 2/7, there is always at least one hydrogen on the methylene, the olefin, and the metallacyclobutane that points away from the PCy_3 ligand and can therefore be substituted by a larger group without imposing additional steric strain. This situation is different for path 3: Especially in the structures TS **1(AB_a)*trans*** and **1(B_a)*trans***, all hydrogen atoms of the olefin point directly toward the cyclohexyl rings of the PCy_3 ligand. Substituting them by a larger group will indeed impose steric strain on those two structures, and as TS **1(AB_a)*trans*** is already the highest point in path 3, it will consequently additionally disfavor path 3 with respect to path 2/7.

Finally, the question of whether the mechanistic picture derived for the first-generation Grubbs-type ruthenium carbene systems can also be applied to the second-generation NHC systems has to be asked. There is now enough experimental^{12,13,20} and theoretical evidence (refs 10, 38 and Table 1) that the phosphane, and not the NHC carbene, dissociates off in the first place, and therefore the intermediates for catalysis by first- and second-generation catalysts are different. There are certainly electronic differences between the NHC and the PCy_3 ligand such as the increased σ donor capability and the reduced π acidity of the NHC ligand,^{72,73,76} but for now only size effects will be discussed, especially as the H_2IMes ligand is considered to be significantly larger than PCy_3 . [This assumption is not necessarily true, as the investigation of solid angle radial profiles (SARP) of PCy_3 and H_2IMes bound to Ru revealed that the SARP_{max} of H_2IMes is only 5–10% larger than that of PCy_3 .⁶⁸]

Consideration of the number of hydrogen atoms that point from the horizontal $\text{Cl-Ru-C}_{\text{carbene}}$ plane upward into the direction of the PCy_3 ligand reveals that in path 2 intermediate **1(B)** has 1 hydrogen pointing into the PCy_3 direction whereas all other pathways have at least 2 hydrogen atoms pointing into the PCy_3 direction. If the H_2IMes ligand was larger than the PCy_3 ligand, intermediate **2(B)** should be raised in energy,

resulting in a higher dissociation barrier for the phosphane in **2(A)**. Yet activation barriers for the alternative pathways would become even more disfavored due to at least two unfavorable steric interactions, and therefore path 2 is also expected to be favored for second-generation NHC ruthenium carbene complexes. This statement, however, remains to be tested. The corresponding energies for the dissociative pathway for **2(A)** are given in Table 1.

An interesting observation can be made if the gas-phase activation energies of **1(B)** and **2(B)** for the reaction with ethylene are compared to those for ethyl vinyl ether and norbornene: They are $\Delta E^\ddagger = -2.6, 1.7,$ and -1.1 kcal/mol for **1(B)** with ethylene, ethyl vinyl ether, and norbornene, respectively, and $\Delta E^\ddagger = -8.8, -5.0,$ and -8.0 kcal/mol for **2(B)**. In both cases, the reaction with ethylene has the smallest activation barrier. In this picture, the observed rates for thermoneutral olefin metathesis reactions by **1** and **2** are not low because they are intrinsically slow, but rather because they are easily reversible, as we have already argued for different rates for the reaction with 1-butene, cyclobutene, cyclopentene, and norbornene.^{14,15}

The Increased Reactivity of Second-Generation Catalysts.

The large increase in phenomenological activity by substitution of a *N*-heterocyclic carbene for a phosphane has recently been explained by a more favorable partitioning of the nascent active species between entry into the catalytic cycle and return to the precatalyst (by rebinding of phosphane) by Grubbs et al.^{12,13,20} on the basis of NMR experiments. There, they have paradoxically found that the activation step, that is, dissociation of one phosphane ligand, in the second-generation catalysts analogous to **2(A)** [the dissociation energies for PCy_3 for the methylene complexes could not be determined due to catalyst decomposition at the experimental conditions (ref 13)] is slower than that for the first-generation systems such as **1(A)**. The slower activation, that is, the step from the precatalyst **(A)** to the activated catalyst **(B)**, is overcompensated by the much better partitioning into the product direction in the second-generation systems. This partitioning issue can be reformulated as the question: Where is the rate-limiting transition state for the overall reaction **(A)** \rightarrow **(G)**?

Recently, we have presented supplementary gas-phase studies on the relative reactivities of **3(B)** and **4(B)** toward ethyl vinyl ether and norbornene.¹⁶ In these studies, the typical activation step, that is, dissociation of PCy_3 from **3(A)** and **4(A)**, has already been anticipated during the generation process of **(B)**, and therefore the observed gas-phase reactivities directly reflect the reactivity of the preformed active species. For **3(B)**, $0.2 \pm 0.1\%$ turnover with ethyl vinyl ether has been observed, while 7.7% of **4(B)** has been transferred to the product **4EVE(F)** and 76% has reached an intermediate state **4EVE(C-E)** indistinguishable by mass alone. Similar results have been obtained for the reaction with norbornene, where 1.8% of ROM(P) product has been formed for **3(B)**, while 88% of ROM(P) product has been observed for **4(B)**.

We have interpreted our results with the typical double minimum potential observed in gas-phase ion molecule reactions: The olefin π complex **(C)** is formed in the gas phase by coordination of the olefinic substrate to the metal center, and if the total energy available for **(C)** in the gas phase was higher than the energy at the incoming asymptote, **(C)** would simply

dissociate again unless a lower exit channel was available. In solution, this excess energy is rapidly dissipated into the medium, but vibrational relaxation can be made much slower in the gas phase.

Considering both the ROMP of norbornene and the acyclic metathesis of ethyl vinyl ether, step (C) \rightarrow (D) has been expected to lie well above the energy of [(B) + olefin] for the first-generation catalyst **3** because both the extent of ROMP of norbornene as well as the extent of either π complex formation or acyclic metathesis of ethyl vinyl ether are very small. On the other hand, the corresponding transition states for **4** have been expected to lie very close to the energy of [(B) + olefin], because both ROMP of norbornene as well as π complex formation and acyclic metathesis of ethyl vinyl ether have been efficient.

Figures 5–8 give the ΔE and $\Delta G_{\text{transl}}^{\circ}$ values for the reaction of **1** and **2** with ethyl vinyl ether and norbornene. In addition, the free energies $\Delta G_{\text{transl}}^{\text{exp}}$ at the actual experimental conditions for the corresponding gas-phase experiments of **3** and **4** are given in square brackets (the $\Delta G_{\text{transl}}^{\text{exp}}$ value for (A) is infinite as there is no PCy₃ available for the reaction (A) \rightarrow (B)). $\Delta G_{\text{transl}}^{\text{exp}}$ is more informative because (i) the gas-phase experiments were performed at low pressure (5–8 mTorr), which leads to an increase of the translational entropy contribution of a factor of ~ 2 as compared to standard state conditions, and (ii) catalytic reactions are usually characterized by a large excess of substrate, rather than by reactants being present at standard state concentrations. For the Grubbs-type ruthenium catalysts, typically 5 mol % (1:20) of catalyst is used for synthetic preparative C=C bond formation steps, and a catalyst-to-substrate ratio of up to 1:1 154 000 has been used in olefin metathesis of 1-octene for a second-generation system.⁵⁹ In the gas phase, the catalyst-to-monomer ratio is a somewhat arbitrary number, but it can be estimated by the number of collisions occurring in the CID cell. This number of collisions has been simulated¹⁵ to be in the range of 10^3 – 10^4 , and, therefore, a K of 5000 has been chosen in the $-RT \ln K$ term. However, using K implies that the gas-phase reactions are in equilibrium and that the rates for the forward and the backward reaction are the same. In reality, the reactions are neither in equilibrium nor have forward and backward reactions of the same rate, as the investigated reactions are strongly exothermic. Therefore, a K of 5000 is only the lower limit, and, consequently, the $\Delta G_{\text{transl}}^{\text{exp}}$ for EVE(C) to EVE(E) and NBE(C) to NBE(F) represents the upper limit and the real free energies may in fact be lower. In solution-phase metathesis, the reactions are usually performed at standard state pressure, and the $\Delta G_{\text{transl}}^{\circ}$ values reduced by a $-RT \ln K$ term for the catalyst-to-substrate ratio (typically 2–5 kcal/mol) are a good approximation.

The computed surfaces that show 6–7 kcal/mol reduced activation barriers for olefin metathesis starting for **2** support to a great extent the interpretation of the gas-phase results.¹⁶ [The experiments were actually performed with benzylidene complexes, while the computations were done on the methylene complexes. This difference significantly accounts for metallacyclobutane formation, where the conjugation of the phenyl with the ruthenium center is broken. For the crucial rate-determining steps before metallacyclobutane formation, critical points on the energy surface have been computed to be identical at ± 1.5 kcal/mol.]

For the reaction with ethyl vinyl ether, 1EVE(C) is higher on the free energy surface than 1EVE(B) and free ethyl vinyl ether, which is in agreement with the low peak intensity of $0.05 \pm 0.03\%$ for and intermediate attributed to 1EVE(C). The intense peak of $76 \pm 0.7\%$ for the olefin π complex in the second-generation systems intermediate is consistent with the ~ 4.2 kcal/mol lower energy of 2EVE(C) as compared to that of 1EVE(C). The 76% of 2EVE(C) also gives rise to an eventual correction of the upper limit of $\Delta G_{\text{transl}}^{\text{exp}}$ for EVE(C) to EVE(E) by ~ -7 kcal/mol. Thereby, 1EVE(C) and TS 1EVE(CD) would still lie well above the free energy of 1EVE(B) and free ethyl vinyl ether, while for 2EVE(C), the second exit channel TS 2EVE(CD) leading to the metallacyclobutane with $\Delta G^{\ddagger} \approx 3.3$ kcal/mol now became available. Although the reactions (B) \rightarrow (A) and (B) \rightarrow (C) have no barrier on the ΔE -surface, there is an entropic barrier for these processes. Grubbs et al.¹³ have found experimentally an entropy of activation of the phosphane exchange of ~ 3.5 kcal/mol, which is about one-third of the upper limit derived by considerations of the entropy changes for translational motions (Figure 9), and a similar value may be expected for (B) \rightarrow (C). Adding this value means, consequently, that at typical experimental conditions for the first-generation system, (C) \rightarrow (D) is rate limiting, while for the second-generation system, (A) \rightarrow (B) is rate limiting.

For the reaction with norbornene, a further observation can be made: The relative fraction of the intramolecular π complex NBE(E) and the 14-electron active species NBE(F) can be experimentally derived from different rates of the first polymerization event and the subsequent events, assuming a preequilibrium between active NBE(F) and inactive NBE(E). Interestingly, for the first-generation complex 3NBE, the subsequent events are accelerated by a factor of 6 over the first propagation step, whereas they are decelerated by a factor of 1.7 for the second-generation complex 4NBE. While this difference may be attributed to changes of the initial benzylidene complex and the propagating alkylidene complex, it is also in agreement with the preference for NBE(E) over NBE(F) in **4** with $\Delta\Delta E = 2.3$ kcal/mol as compared to **3** with $\Delta\Delta E = 0.6$ kcal/mol. However, for a σ donor trans to the PCy₃ or H₂IMes, this preference may be reversed.⁵⁵

The computational results, which show a reduced barrier for metallacyclobutane formation in the second-generation systems, are in total agreement with Grubbs et al.'s NMR experiments,¹³ where they have observed saturation conditions for the analogues of **2** but not for the analogues of **1**, meaning that for **1**, step (C) \rightarrow (D) was rate limiting, whereas for **2**, step (A) \rightarrow (B) was rate limiting. Of course, at specific experimental conditions (low temperatures or high concentrations of substrate), step (A) \rightarrow (B) can become also rate limiting for **1**, as has been observed by Lehman and Wagner,²² where at low temperatures (PCy₃)₂-Cl₂Ru=CHPh was faster in ADMET of 1,9-decadiene than was (H₂IMes)(PCy₃)Cl₂Ru=CHPh.

It turns out that the introduction of an *N*-heterocyclic carbene into the ruthenium carbene system significantly increases the catalyst commitment¹⁶ by both lowering the potential for the formation of metallacyclobutane and coincidentally raising the energy of the 14-electron active species. While for near-thermoneutral-reactions the ligand symmetry may partly account for the observed increase in rate,⁴⁰ this explanation cannot hold for the more exothermic reactions where TS (C) \rightarrow (D) is far

above TS (**D**) \rightarrow (**E**). Cavallo³⁸ has suggested that steric interaction of the carbene with the NHC ligand destabilizes the 14-electron complex over the metallacyclobutane and therefore accelerates the reaction, but a (reduced) destabilization has also been found for the IH^{39} and the H_2IH model systems that cannot exhibit considerable steric effects. Electronically, however, there is a big difference between the 14-electron four-coordinate active species (**B**), the 16-electron intermediate (**C**), and the 14-electron metallacyclobutane (**D**). Especially (**D**), that exhibits no extra conjugative stabilization via the carbene, is expected to be destabilized by electron-withdrawing groups, and therefore a decreased rate according to Hammond's postulate⁷⁸ is expected, as has been computationally confirmed for the phenyl and ethoxy residues on the metallacyclobutane. Similar trends are also found for the computed energies of the PH_3 , PMe_3 , and PCy_3 model complexes, where destabilization of the metallacyclobutane by the stronger π acid and stabilization by the stronger σ donor are observed. The NHC ligand itself is a weak π acid and a strong σ donor in extremis and therefore leads to the greatest rate enhancements in metallacyclobutane formation.

Along these lines, improvement of catalyst commitment¹⁶ for the first-generation systems may also be achieved by a more weakly π acidic phosphane such as tripyrrolidinophosphane. For second-generation systems, the most weakly π acidic triazolylidene complexes indeed give the highest rates.⁸³ Unfortunately, the triazolylidene complexes are unstable in solution.

Conclusion

A large set of possible pathways for the mechanism of olefin metathesis by the first-generation ruthenium carbene complexes **1(A)** has been studied on the complete system, including all relevant transition states. The investigations reveal the trans

dissociative pathway 2/7 as the most favorable one. While on the ΔE -surface the trans dissociative and the trans associative paths are comparable, the former is favored by at least 9 kcal/mol on the ΔG -surface due to the gain of translational entropy in the dissociation step. The trans dissociative path is also believed to be the favored one for the second-generation NHC ruthenium carbene catalysts, and it also applies for olefin metathesis by Hofmann-type ruthenium carbene systems.

For exergonic reactions with ethyl vinyl ether and norbornene, release of excess energy takes place in the [2+2] cycloreversion step (**D**) \rightarrow (**E**), and the reactions become irreversible. Almost thermoneutral reactions as in the case of ethylene are highly reversible, and their reverse reaction rate accounts for their low reactivity, while their reaction rate in the forward reaction may even be higher.

The theoretical results reproduce to quite an extent the experimental results if experimental conditions are taken into account for the free energy surface. Under typical reaction conditions, for the first-generation catalysts, metallacyclobutane formation is the rate-limiting step, whereas for the second-generation catalysts, generation of the active species by dissociation of one (phosphane) ligand is rate limiting.

The different partitioning toward the products in the first- and second-generation ruthenium carbene complexes is mostly caused by their different stability for the 14-electron carbene species with respect to the 14-electron metallacyclobutane intermediate. This is to a great extent due to electronic effects, while steric differences, in particular between PCy_3 and $\text{H}_2\text{-IMes}$, play a minor role.

Supporting Information Available: Computational details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA0305757

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