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Comparative DFT study on the role of conformers in the ruthenium alkylidene-catalyzed ROMP of norborn-2-ene

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Comparative quantum chemical calculations on the reaction pathways for the formation of ruthena(IV)cyclobutanes from both 1st- and 2nd-generation Grubbs catalysts of the general formula $RuX_2(L)(L')({=}CH_2)$ ($L = PCy_3$ or 1,3-dimesityl-4,5-dihydroimidazolin-2-ylidene, $L' = PCy_3$) and norborn-2-ene (NBE) were carried out on the B3LYP/LACVP level in dependence on the ligand X = I, Br, Cl, and F. The mechanism proposed by Straub for the formation of (one) active and (three) inactive NBE–Ru–carbene complexes for non-cyclic alkenes was applied to the cyclic alkene NBE. In $RuX_2(PCy_3)_2({=}CH_2)$, the inactive NBE–Ru–carbene complex is energetically more stable than the active one; however, in $RuX_2(IMesH_2)(PCy_3)({=}CH_2)$, the active NBE–Ru–carbene complex is more stable than the inactive one. In due consequence, the possible rate limiting barrier for the conversion of the NBE–Ru–carbene complex into the corresponding metallocyclobutane (MCB) is systematically larger in the case of 1st-generation Grubbs catalysts than of 2nd-generation Grubbs catalysts due to an additional re-arrangement for the formation of an active π-complex from the more stable (inactive) conformer. This correlates with the observed reactivity of both types of initiators. There is a strong influence of the ligands L and X on the conformational properties and relative stabilities of the 14-electron intermediates, which has a direct effect on the distribution of the inactive and active conformations of the corresponding Ru–carbene–NBE complexes. A direct correlation between the conformational properties of the 14-electron intermediates and the relative stabilities of the active Ru–carbene–NBE complexes was observed. Copyright © 2008 John Wiley & Sons, Ltd.**

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Keywords: quantum chemical calculations; ruthenium; alkylidenes; Grubbs catalysts; ring-opening metathesis polymerization (ROMP)

INTRODUCTION

Olefin metathesis[1–4] is a fundamental reaction for the formation of carbon–carbon double bonds. The developments in that area of chemistry are strongly related to catalyst development[5] and have finally been acknowledged with the Chemistry Nobel Price in 2005.[6–8] In terms of polymer chemistry, Grubbs initiators have been widely used for acyclic diene metathesis (ADMET) polymerization,[9] ring-opening metathesis polymerization (ROMP),[10] and even cyclopolymerization of 1,6-heptadiynes.[11] Reactivity of the "*1st-generation*" Grubbs-catalysts $RuX_2(PCy_3)_2({=}\,CH_2)$ (X = Cl, Br, I) for many metathesis reactions was significantly improved by introducing the "*2nd-generation*" Grubbs-catalysts $RuX_2(PCy_3)(IMesH_2)({=}CH_2)$ (X = Br, Cl, I, $IMesH_2$ = 1,3-dimesityl-4,5-dihydroimidazol-2-inylidene), where an N-heterocyclic carbene (NHC) replaces one phosphane group.[12–18] Because of their stability and the ease of handling, both Ru-based catalysts and the mechanism of olefin metathesis by ruthenium carbene complexes were the subject of intense experimental[19–28] and detailed computational studies.[18,29–46] From the results of comprehensive calculations on the mechanism of olefin metathesis[19,29] it was concluded that for 2nd-generation Grubbs catalysts, the formation of the 14-electron active species via the dissociation of phosphane is rate limiting, whereas for 1st-generation Grubbs catalysts the barrier for metallocyclobutane (MCB) formation is the rate limiting step. The origin of the high activity of 2nd-generation Grubbs catalysts in alkene ($CH_2{=}CH_2$) metathesis was also studied quantum chemically by Straub.[47–49] It was proposed that the key to the understanding of metathesis activities is the existence of active and inactive conformers in the alkene–Ru–carbene intermediates, where the high reactivity of 2nd-generation Grubbs catalysts originates mainly from the electronic stabilization of the active carbene conformation by the NHC ligands. Despite this impressive theoretical work on Grubbs initiators, whether related to olefin metathesis reactions such as cross-metathesis and ring-opening cross-metathesis or to ROMP, there is still considerable demand for theoretical investigations, particularly for metathesis reactions related to ROMP or cyclopolymerization. The aim of the present work was: (i) to prove the applicability of the mechanism

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Table 1. Relative energies ΔE, $\Delta E_0(E + \text{ZPE})$ and ΔG (kcal mol^{-1}) of different structures of Ru-complexes, calculated relative to the most stable structure (*A*) of the pre-catalysts $\text{RuX}_2(\text{PCy}_3)\text{L}({=}\text{CH}_2)$

L ligand		PCy_3	PCy_3	PCy_3	PCy_3	IMesH_2	IMesH_2	IMesH_2	IMesH_2
X ligand		X = I	X = Br	X = Cl	X = F	X = I	X = Br	X = Cl	X = F
$\Delta H^{\ddagger}$ [24]		19.0 ± 0.5	23.1 ± 0.3	23.6 ± 0.5		23 ± 4	27 ± 2	27 ± 2	
B(par)	ΔE	17.2	23.2	22.8	24.4	18.3	25.0	25.7	25.0
	ΔE^{a}	15.2	21.3	21.3	21.1	15.8	22.0	22.7	22.0
	ΔE_0^{b}	15.5		20.6				22.9	
	ΔG	-0.4	7.3	7.4	8.8	0.5	5.9	9.5	8.1
B(ort)	ΔE	27.0	32.1	33.6	45.0	21.9	27.6	29.3	37.8
	ΔE_0	23.9	28.8	30.6	41.8	18.7	25.4	26.3	35.0
	ΔG	8.6	15.6	17.5	27.8	4.7	9.0	13.3	19.5
C(i;i)	ΔE	15.5	16.9	16.2	12.5	18.6	21.4	20.6	15.4
inactive	ΔE_0	15.1	18.1	17.4	12.9	17.4	21.2	19.5	16.2
	ΔG	12.2	15.6	14.4	11.9	15.9	17.0	19.2	13.1
C(i;a)	ΔE	15.9	16.6	16.4	20.5	15.3	15.9	15.3	17.3
inactive	ΔE_0	15.6	17.1	17.3	20.7	15.4	16.4	15.6	18.0
	ΔG	13.8	17.7	14.7	19.6	13.4	13.4	14.5	16.1
D(a;i)	ΔE	16.5	17.9	16.3	13.8	17.9	21.6	20.8	14.1
inactive	ΔE_0	16.6	18.2	17.2	14.1	17.2	21.6	20.3	16.6
	ΔG	12.3	15.8	13.4	12.1	14.4	14.4	18.1	12.1
D(a;a)	ΔE	18.1	18.6	18.2	20.9	16.3	17.1	16.1	15.9
active	ΔE_0	17.4	18.5	16.4	20.1	16.3	17.4	15.9	16.5
	ΔG	13.7	16.4	16.2	19.5	12.5	13.7	16.1	13.4
TS	ΔE	20.9	20.8	19.8	22.1	19.1	19.7	17.9	16.3
	ΔE_0	22.0	20.5	17.7	21.5	18.8	19.7	17.3	16.4
	ΔG	19.6	20.5	19.9	20.8	18.6	17.3	19.3	15.2
MCB	ΔE	11.9	11.3	9.2	8.3	9.0	6.8	5.0	1.6
	ΔE_0	12.6	12.7	8.8	9.6	8.6	8.0	5.9	3.8
	ΔG	12.4	13.2	11.5	7.7	8.4	6.7	8.4	3.0

$\Delta H^{\ddagger}$ (kcal mol^{-1}) – experimental enthalpy of activation of PCy_3 dissociation; ΔE^{a} (this work) and ΔE_0^{b} (Straub[47]) – calculated at the B3LYP/LACV3P**+//LACVP** level of theory.

proposed by Straub for the ROMP of norborn-2-ene (NBE); (ii) to study the proposed rate limiting barriers for the conversion of the π-complex into the MCB in dependence on the ligands L (L = PCy_3, IMesH_2) and X (X = F, Cl, Br, and I); (iii) to compare the influence of the ligands L and X on conformational properties of the 14-electron intermediates and their effect on the distribution of the inactive and active conformations of Ru–carbene–NBE intermediates, and, finally, (iv) to correlate these results with existing experimental data. $\text{RuX}_2(\text{PCy}_3)_2({=}\text{CH}_2)$ and $\text{RuX}_2(\text{IMesH}_2)(\text{PCy}_3)({=}\text{CH}_2)$ were chosen as model systems because these systems have been studied extensively both experimentally and theoretically.

COMPUTATIONAL METHODS

Density Functional Theory (DFT) calculations were carried out using Becke's three-parameter functional (B3)[50,51] in combination with the Lee, Yang, and Parr (LYP) correlation functional.[52] The molecular geometries of all calculated molecules were optimized at the B3LYP/LACVP** (Jaguar version 6.5 program[53]) level. The LACVP** basis set uses the standard 6-31G** basis set for light elements and the LAC pseudopotential[54] for third-row and heavier elements. This method was successfully used for the computational modeling of ruthenium alkylidene mediated olefin metathesis.[34,55] Recently, we demonstrated the applicability of this method by calculating carboxylate-substituted Schrock catalysts and comparing the computational results with X-ray structural data.[56] The B3LYP/LACV3P**+//B3LYP/LACVP** level of theory, which was successfully used for the calculation of the relative energies of catalytic intermediates,[47] was used in some cases for comparison and revealed results that were very similar to those obtained at the B3LYP/LACVP** level (Table 1 and Fig. 4(a)). The most stable structures of the PCy_3 ligand and of the 1st- and 2nd-generation catalysts in dependence on the X ligands are given in the Supporting Information, Fig. 1(S). It is also worth mentioning that the structures of the Ru–methylidene–NBE complexes calculated in this work are also in very good agreement with the reported full DFT BP86 geometries.[29] To test the reliability of the B3LYP functional, the relative energies of the different conformers were also calculated with MPW1K[57] and X3LYP[58] DFT methods as implemented in the Jaguar version 6.5 program. The MPW1K method is optimized against a database of 20 forward barrier heights, 20 reverse barrier heights, and 20 energies of reaction. It reduces the mean unsigned error in the reaction barrier height by a factor of 3 compared to the B3LYP one. The X3LYP method improves the accuracy in heats of formation, ionization potential, electron affinities, and total atomic energies compared to the B3LYP one. However, a comparison of the results obtained with these methods (Fig. 4(a)) revealed very similar qualitative and quantitative trends, indicating the reliable applicability of the B3LYP method to the current problem. Frequency calculations were done at the same level of theory to characterize the stationary points on the potential surface and to obtain zero point energies (ZPE) and Gibbs free energy (G) at a standard temperature of 298.15 K and a pressure of 1 atm using unscaled vibrations. The relative stabilities of the different complexes were calculated as the difference of the electronic energies ΔE, total electronic energies $\Delta E_0 (E_0 = E + \mathrm{ZPE})$ and Total Gibbs free energies ΔG between reactants and products relative to the most stable conformer of the pre-catalysts (structure A(ort) or A(par)).

RESULTS AND DISCUSSION

Adopting the *trans*-dissociative pathway[39,59] for MCB formation as the most favorable one[29] and applying the proposed model of active and inactive conformations developed by Straub[47,49] to NBE, the structures and relative energies of different conformers (Fig. 1) were systematically analyzed in dependence of the ligands L (PCy_3, $IMesH_2$) and X (F, Cl, Br, I).

The relative energies (relative to the most stable structure (A) of the catalyst) of the different structures are summarized in Table 1. The computed dissociation energies for PCy_3 in the cases of X = I, Br, Cl agree well with the experimental values of the enthalpy of activation of phosphane dissociation for the corresponding benzylidene complexes in 1st- and 2nd-generation Grubbs catalysts.[23,24]

It should be noted that for both 1st- and 2nd-generation Grubbs catalysts, *two possible conformers with the carbene moiety* (*i.e., the Ru—C—H plane*) *either nearly parallel or orthogonal to the* CH_2*=Ru-L plane* (*L* = PCy_3, $IMesH_2$) *can be calculated.* In all cases, the most stable structures of the 1st- and 2nd-generation Grubbs catalysts have carbene moieties nearly orthogonal to the CH_2=Ru-L plane (except in the case of L = PCy_3 and X = F, where the structures with the carbene moieties nearly parallel to the CH_2=Ru-L plane were found to be the more stable ones). Only the most stable structures of the 1st- and 2nd-generation Grubbs catalysts are shown in Figs Figures 2 and 5. The calculated energy difference between the two conformers in both types of initiators ranges from 1.4 to 7.0 kcal mol^{-1} in dependence on the L and X ligands and suggests that the rotation of the carbene moiety, which has been proposed to proceed freely,[29] might be hindered to some extent. It can be seen that the computed dissociation energy for PCy_3 is systematically lower in 1st-generation Grubbs catalysts than it is in 2nd-generation ones. Thus, in agreement with experiments,[23,24] the first activation step, i.e., dissociation of one phosphane ligand, is slower in 2nd-generation Grubbs catalysts since it requires a larger dissociation energy.

Using the concept of active and inactive Ru–carbene–NBE complexes,[47–49] the four possible Ru–carbene–alkene complexes C(i;i), C(i;a), D(a;i), and D(a;a) (Fig. 1) were optimized. In these abbreviations, "a" and "i" refers to the "active" and "inactive" complex conformations. The two conformers C(i;i) and C(a;i) are inactive because of an unfavorable orientation of the NBE double-bond (orthogonal) relative to the Ru–carbene, preventing any significant orbital overlap. It should be noted that in the cases where L = $IMesH_2$ and X = I, Br, Cl, the inactive conformations of C(i;i) could only be optimized as a transition state for methylidene rotation (it has one negative frequency). In the D(a;i) structure, the NBE is oriented in a nearly parallel way to the inactive Ru–carbene, which is parallel to the CH_2=Ru-L plane. Thus, only the D(a;a) conformer, with the NBE fairly parallel to the Ru–carbene (calculated dihedral angles are 29 and 31° in the case of X = Cl and L = $IMesH_2$ or PCy_3, respectively) and an active carbene orientation orthogonal to the CH_2=Ru-L plane is active for immediate transformation into MCB. From this analysis of the four possible alkene–Ru–carbene complexes C(i;i), C(i;a), D(a;i), and D(a;a) follows that direct formation of the MCB is only possible from the active structure D(a;a) via the transition structure (TS) (shown in Fig. 1). As follows, the relative stability of the active D(a;a) should also play an important role for the efficiency of the catalyst. For the transformation of the structures

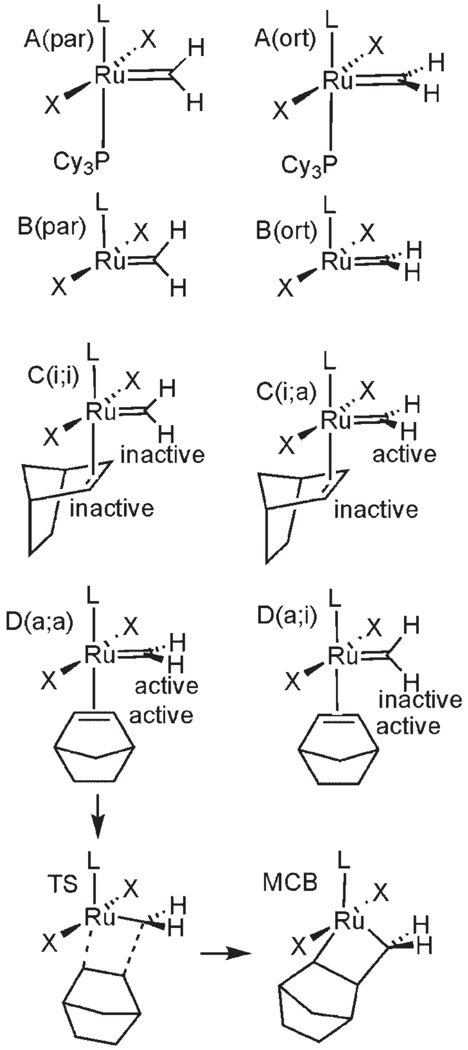

Figure 1. Structures of studied complexes

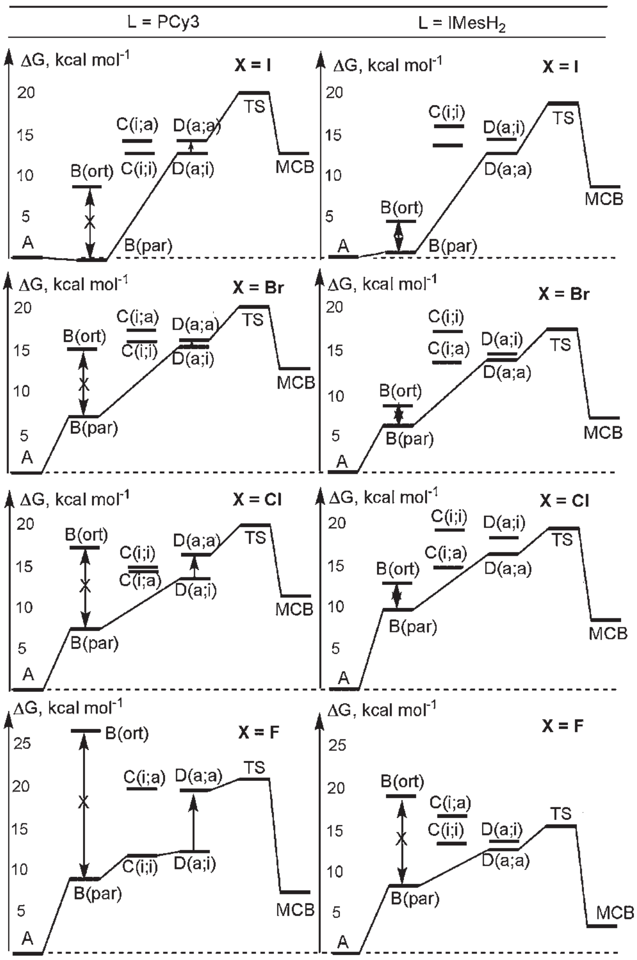

Figure 2. Relative total Gibbs free energies ΔG (kcal mol^{-1}) for the reaction of 1st- and 2nd-generation Grubbs catalysts with NBE in dependence on the X ligands (values from Table 1)

C(i;i) and C(i;a) into active D(a;a), a sterically hindered rotation of NBE is required. However, the transformation of the complexes C(i;i) and C(i;a) into the corresponding complexes D(a;i) and D(a;a) occurs with low activation energy. As calculated, the activation energy for the transformation through NBE rotation of the inactive complex C(i;a) into the corresponding active complex D(a;a) is only 2.5 and 3.0 kcal mol^{-1} for X = Br and L = PCy$_3$ and IMesH$_2$, respectively, and 3.6 kcal mol^{-1} for X = Cl and L = IMesH$_2$. That is in agreement with an assumed free rotation of the coordinated olefin.[29] The relative Gibbs free energies ΔG for the reaction of 1st- and 2nd-generation Grubbs catalysts with NBE in dependence on X ligands are shown in Fig. 2, the relative energies ΔE are given in the Supporting Information Fig. 2(S)). In due consequence, there may be no strong driving force for the fast transformation of inactive C(i;i) and C(a;i) into the corresponding structures D(a;i) or D(a;a) with similar energy. Thus, to understand the difference in catalytic activity between 1st- and 2nd-generation Grubbs catalysts in dependence on the X ligand, we analyzed the alkene–Ru–carbene complexes D(a;i) and D(a;a) as well as the activation energy for MCB formation more closely. It is worth mentioning that the active Ru–methylidene–NBE complex D(a;a) can be localized, which is in contrast to reactions involving acyclic alkenes (ethylene).[45]

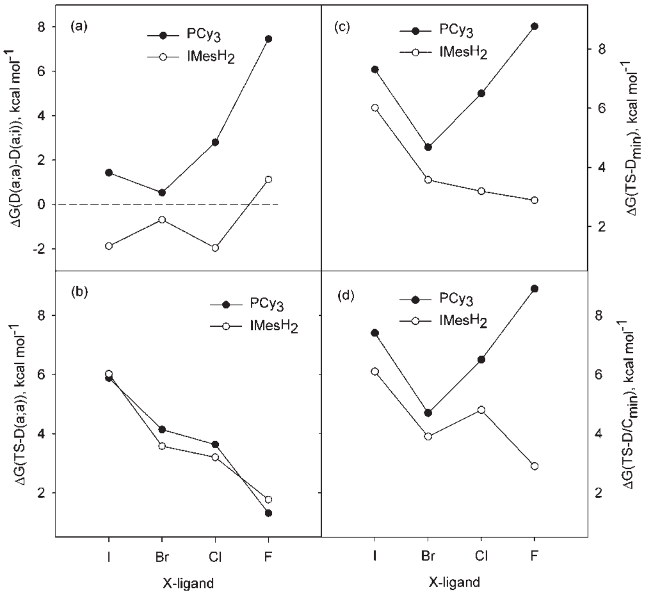

Figure 3. Comparison of calculated total Gibbs free energies (kcal mol^{-1}) for 1st- and 2nd-generation Grubbs catalysts in dependence on the L and X ligands: (a) difference of Gibbs free energies ΔG(D(a;a) – D(a;i)) between the inactive and active Ru–carbene–NBE complexes; (b) difference of Gibbs free energies ΔG(TS – D(a;a)) between the transition structure TS and the active Ru–carbene–NBE complex D(a;a); (c) difference of Gibbs free energies ΔG(TS – D$_{min}$) between the transition structure TS and the most stable Ru–carbene–NBE complex D(a;i or a;a); (d) difference of Gibbs free energies ΔG (TS – D/C$_{min}$) between the transition structure TS and the most stable structures (Ru–carbene–NBE complexes D or C)

In this context, the first striking difference between 1st- and 2nd-generation Grubbs catalysts is the relative stability of both the D(a;i) and D(a;a) complex. In the case of RuX$_2$(PCy)$_3$(=CH$_2$) derived catalysts, the inactive structure D(a;i) is systematically more stable than the active structure D(a;a). In contrast, the active structure D(a;a) derived from RuX$_2$(IMesH$_2$)(PCy$_3$)$_2$(=CH$_2$) is more stable for X = I, Br, and Cl, and only slightly less stable for X = F, indicating the better stabilization of the active carbene moiety conformation (*carbene moiety nearly orthogonal to the* CH_2*=Ru-L plane*) due to the IMesH$_2$ ligand. Thus, the formation of the MCB can proceed in one step from D(a;a) into the MCB in 2nd-generation Grubbs catalysts. In contrast, in 1st-generation Grubbs catalysts, the formation of the MCB from D(a;i) needs an additional re-arrangement, i.e., the rotation of the methylidene group. The energy differences between the structures D(a;i) and D(a;a), differences between the TS and active D(a;a), differences between the TS and the most stable structure D(a;i or a;a), and differences between the TS and the most stable structure of the Ru–methylidene–NBE complex are summarized in Table 2. Differences in the Gibbs free energies in dependence on the X ligands are shown in Fig. 3. It is worth notifying that in 1st-generation Grubbs catalysts, the energy difference between the structures D(a;i) and D(a;a) is always positive (Fig. 3(a)). However, it is negative for the 2nd-generation Grubbs catalysts with X = I, Br, and I.

The calculated energy barrier for the transformation of active D(a;a) into a MCB (energy difference between the TS and D(a;a)) is very similar for both 1st- and 2nd-generation Grubbs catalysts. However, it depends clearly on the X ligands. In both catalyst

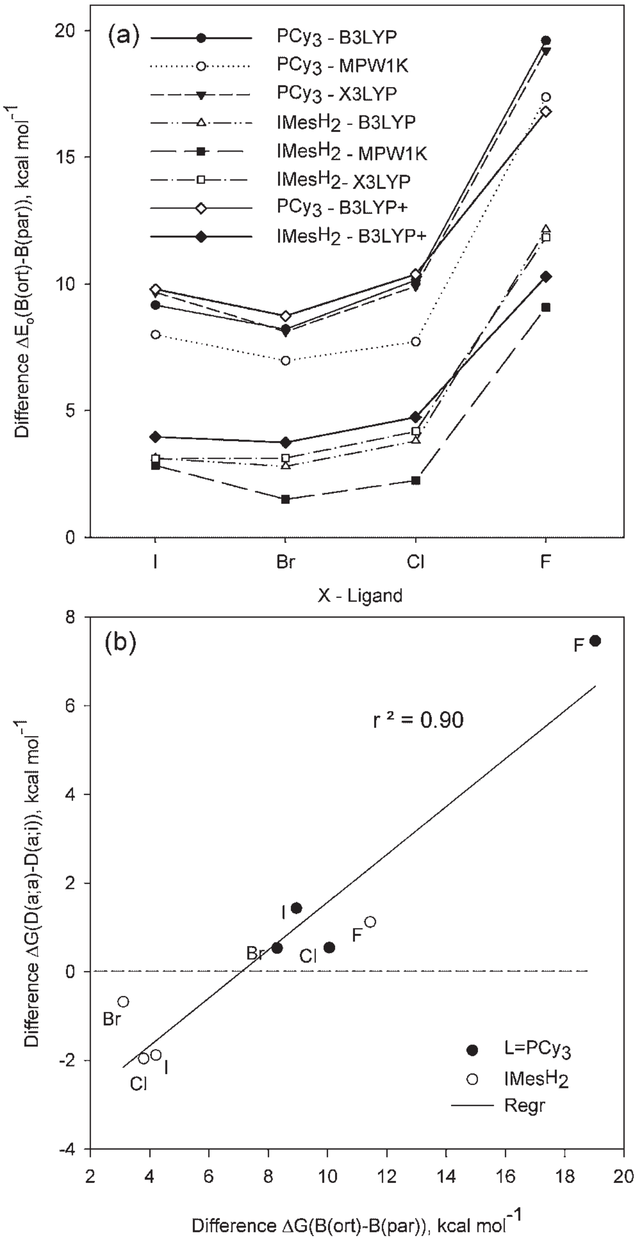

Figure 4. (a) Dependence of the total electronic energy difference ΔE_0 between two conformers B(ort) and B(par) of an 14-electron intermediate on the X and L ligands and the DFT method used for calculation (B3LYP+ used LACV3P**+ basis set at geometry optimized with LACVP**); (b) correlation between the difference in Gibbs free energies ΔG between two conformers B(ort) and B(par) and ΔG between the active D(a;a) and the inactive D(a;i) Ru–carbene–NBE complexes. Here, the zero line corresponds to an equal relative stability of D(a;a) = D(a;i)

systems, the largest barrier was found for X = I and the lowest for X = F (Fig. 3(b)). Thus, in case the additional step for transformation of inactive D(a;i) into D(a;a) in 1st-generation Grubbs catalysts is taken into account, the difference between 1st- and 2nd-generation Grubbs catalysts is pronounced and particularly large for X = Cl and F (Fig. 3(c)). Moreover, due to a very small energy difference between the most stable structure C and the corresponding D complexes, the differences in Gibbs free energies $\Delta G(\mathrm{TS} - \mathrm{D_{min}})$ follow a similar trend as for $\Delta G(\mathrm{TS} - \mathrm{D/C_{min}})$ (compare Fig. 3(c) and 3(d)). As follows, the overall barrier for the conversion of the most stable π-complex ($\mathrm{D_{min}/C_{min}}$, identified by Sanford *et al.*[24] as a resting state) into the MCB is systematically higher in the case of 1st-generation Grubbs catalysts. That is in agreement with calculations[29] on the reaction pathway for MCB formation for the reaction 1st- and 2nd-generation Grubbs catalysts with NBE in the case of X = Cl. *In due consequence, despite the easier phosphane dissociation, the calculated significant difference in the overall barrier for the conversion of the π-complex into the MCB agrees well with the observed lower reactivity of 1st-generation Grubbs catalysts compared to 2nd generation Grubbs catalysts.*

For the better understanding of active D(a;a) complex formation, we concentrated on the properties of the active 14-electron intermediate, which is formed after dissociation of the phosphane. Two conformers of the 14-electron intermediate with the carbene unit nearly parallel and orthogonal to the $\mathrm{CH_2{=}Ru\text{-}L}$ plane (structure B(par) and B(ort)) should therefore be analyzed in dependence of the ligands L and X. Analysis of the two different conformers of the 14-electron intermediate in 1st-generation Grubbs catalysts reveals the existence of only one stable conformer with the carbene unit nearly parallel to the $\mathrm{CH_2{=}Ru\text{-}L}$ plane (structure B(par)). The second structure B(ort) is only a transition state. In the case of 2nd-generation Grubbs catalysts and for X = I and F, again only one conformer B(par) represents a stable structure. However, in the cases of X = Cl and Br, two stable conformers, B(par) and B(ort), were localized during optimization, with B(par) being the more stable one. The calculated activation energy for rotation from the local minimum B(ort) into the absolute minimum B(par) is very small ($<0.5\,\mathrm{kcal\,mol^{-1}}$ for X = Br, Cl). The calculated relative energies of both conformers in dependence on the ligands L and X are given in Table 1. As can be seen, there is a very strong effect of both the L and X ligands on the relative energy of the two conformers B(par) and B(ort). Energy differences between the two conformers are systematically larger in the case of the 1st-generation Grubbs catalysts. For both types of catalysts, the largest energy difference was calculated for X = F. The relative stabilities of the two conformers calculated with the B3LYP method agree well with those calculated with the alternative DFT method MPW1K and X3LYP. The differences in Gibbs free energies between the two conformers B(par) and B(ort) in dependence on both the L and X ligands and DFT method used are shown in Fig. 4(a).

While in the case of L = $\mathrm{IMesH_2}$ and X = Cl or Br the 14-electron intermediate B(ort) is only a local minimum, it can transform through rotation (calculated for stable B(ort) structure frequency of rotation $\sim 200\,\mathrm{cm^{-1}}$, $t = 1.6 \times 10^{-13}\,\mathrm{s}$) into a more stable conformer with the carbene unit parallel to the $\mathrm{CH_2{=}Ru\text{-}L}$ plane. It may well be assumed that in the case of small energy differences (small barriers, ΔE approx. $<5\,\mathrm{kcal\,mol^{-1}}$), the free rotation of the carbene occurs at room temperature. In due consequence, a continuous distribution of all possible conformers, i.e., parallel and orthogonal, should exist. However, for large energy differences ($\Delta E > 5\,\mathrm{kcal\,mol^{-1}}$), as is the case in 1st-generation Grubbs catalysts (especially for X = F), the formation of structures with the carbene unit orthogonal to the $\mathrm{CH_2{=}Ru\text{-}L}$ plane seems to be impossible. In contrast, both conformers will be populated in 2nd-generation Grubbs catalysts due to the small energy difference between the conformers at room temperature and above (especially for X = Br, Cl with energy difference 2.8 and $3.8\,\mathrm{kcal\,mol^{-1}}$ respectively).

Table 2. Total Gibbs free energy difference ΔG (kcal mol^{-1}) between different structures of Ru-complexes (shown in Fig. 1 and Table 1) in dependence on both the L and X ligands. D_{min}: energetically most stable structure from D(a;a) and D(a;i)

L ligand		PCy_3	PCy_3	PCy_3	PCy_3	$IMesH_2$	$IMesH_2$	$IMesH_2$	$IMesH_2$
X ligand		X = I	X = Br	X = Cl	X = F	X = I	X = Br	X = Cl	X = F
B(ort) – B(par)	ΔG	9.0	8.3	10.1	19.0	4.2	3.1	3.8	11.4
D(a;a) – D(a;i)	ΔG	1.4	0.6	2.8	7.4	– 1.9	– 0.7	– 2.0	1.1
TS – D(a;a)	ΔG	5.9	4.1	3.6	1.3	6.0	3.6	3.2	1.8
TS – D_{min}	ΔG	7.3	4.7	6.5	8.8	6.1	3.6	3.2	2.9
TS – $(D/C)_{min}$	ΔG	7.4	4.7	6.5	8.9	6.1	3.9	4.8	2.9

Analysis of geometries and frontier molecular orbitals of both conformers of the 14-electron intermediate shows that reaction of the conformer having the carbene unit parallel to the $CH_2{=}$Ru-L plane with NBE leads to the formation of the inactive D(a;i) complex, which should transform through methylidene group rotation into the active D(a;a) complex for further formation of the MCB. Otherwise, the conformer with the carbene unit orthogonal to the $CH_2{=}$Ru-L plane is prone to the direct formation of the active complex D(a;a), followed by fast transformation into the MCB due to a small (*ca.* <3 kcal mol^{-1}) barrier (energy difference between structures TS and D(a;a)). Using thermochemical parameters calculated by frequency analysis, i.e., reaction entropy and enthalpy, it is possible to estimate the relative concentration of both the most stable B(par) and the less stable B(ort) conformer. These calculations reveal that in the case of 2nd-generation Grubbs catalysts with X = Cl, the concentrations of the B(ort) conformer are 0.2% at 300 K, 0.5% at 350 K, and 0.7% at 380 K. In the case of X = Br, the estimated concentration of B(ort) is even larger, i.e., 1% at 300 K, 2% at 350 K, and 2.5% at 380 K. However, especially in the case of 2nd-generation Grubbs catalysts, which display small differences in energy between the conformers (X = Br, Cl), the direct formation of the active D(a;a) complex from the 14-electron intermediate could be an effective pathway. This may therefore well be expected to enhance catalytic activity and in due consequence lead to faster polymer formation compared to 1st-generation Grubbs catalysts. These data are of particular interest to polymer chemists, since they are in agreement with the poor initiation efficiencies (typically <5%) observed in 2nd-generation Grubbs catalysts of the general formula $RuCl_2$(IMesH$_2$)(PCy$_3$)(CHR).[60] It should be mentioned that in the case of a catalyst based on a substituted carbene (e.g., CHPh), the conformer B(ort) will be less stable compared to B(par). Test calculations showed that again the energy differences between the two conformers are systematically larger in the case of the 1st-generation Grubbs catalysts (8 and 12 kcal mol^{-1} for X = Br and L = IMesH$_2$ or PCy$_3$, respectively) indicating better stabilization of the orthogonal structure with IMesH$_2$.ligand.

Of further interest was a comparison of the energy difference between the active D(a;a) and inactive D(a;i) complex with the energy difference between the two B(par) and B(ort) conformers of the 14-electron intermediate. It can be seen (Fig. 4(b) for Gibbs free energies), that there is a clear correlation (correlation coefficient $R^2 = 0.90$) between these two parameters. The smaller the energy difference between the two B(par) and B(ort) conformers of the 14-electron intermediate, the more stable is the active D(a;a) complex. Moreover, in case the energy difference between the two B(par) and B(ort) conformers is small, the active D(a;a) complex will be more stable than the inactive D(a;i) complex (energy difference between D(a;i) and D(a;a) is negative). A comparison of the data from the calculated correlation (Fig. 4(b)) with experimentally determined catalytic activities of different 1st- and 2nd-generation Grubbs catalysts further supports this correlation. The data for the most reactive catalyst are below the zero line (defined as D(a;a) = D(a;i)), while the data for the less reactive catalyst are above. Thus, in agreement with the experiment, 1st-generation Grubbs catalysts with X = F turn out to be the least reactive ones, while 2nd-generation Grubbs catalysts with X = I, Br, and Cl are the most reactive ones.

On the basis of these data, the large increase in reactivity observed by substitution of one phosphane ligand by an NHC can be explained by a more favorable partitioning of the active species after entering the catalytic cycle. These findings can be used to create a more general model (Fig. 5).

Thus, the slower activation in 2nd-generation Grubbs catalysts is a result of the higher dissociation energy of the phosphane ligand. This is over-compensated by a much lower barrier for transformation from the most stable Ru–methylidene–NBE complex (resting state) through the active D(a;a) complex into the MCB. The higher barrier for the transformation into the MCB in the case of 1st-generation Grubbs catalysts stem from the necessary additional re-arrangement for formation of the active D(a;a) complex structure from the more stable, yet inactive D(a;i) complex. In the case of 2nd-generation Grubbs catalysts with X = I, Br, and Cl, a reduced energy difference between the two B(par) and B(ort) conformers generally correlates with an enhanced stability of the active D(a;a) complex. The comparably low reactivity in the case of X = I may be explained by the very low reaction enthalpy of Ru–carbene–NBE complex formation (very weak complex) and a still relatively large barrier for transformation into the MCB (energy difference $\Delta G(TS - D/C_{min})$, Fig. 3(d)). As can be seen (Table 2 and Fig. 3(b)) the calculated barrier for transformation of the active D(a;a) complex into the MCB correlates with the experiments,[24] where exchange of the X ligand by I, Br, or Cl resulted in an increase in reactivity. The lower the barrier, the more active is the catalyst. Moreover, the D(a;a) complexes are systematically more stable in the case of 2nd-generation Grubbs catalysts. As also observed experimentally, the really large increase in reactivity of 2nd-generation Grubbs catalysts may be expected in the cases of X = Cl and Br, which also possess a reasonable possibility to populate the orthogonal conformer B(ort). That could apparently lead to a

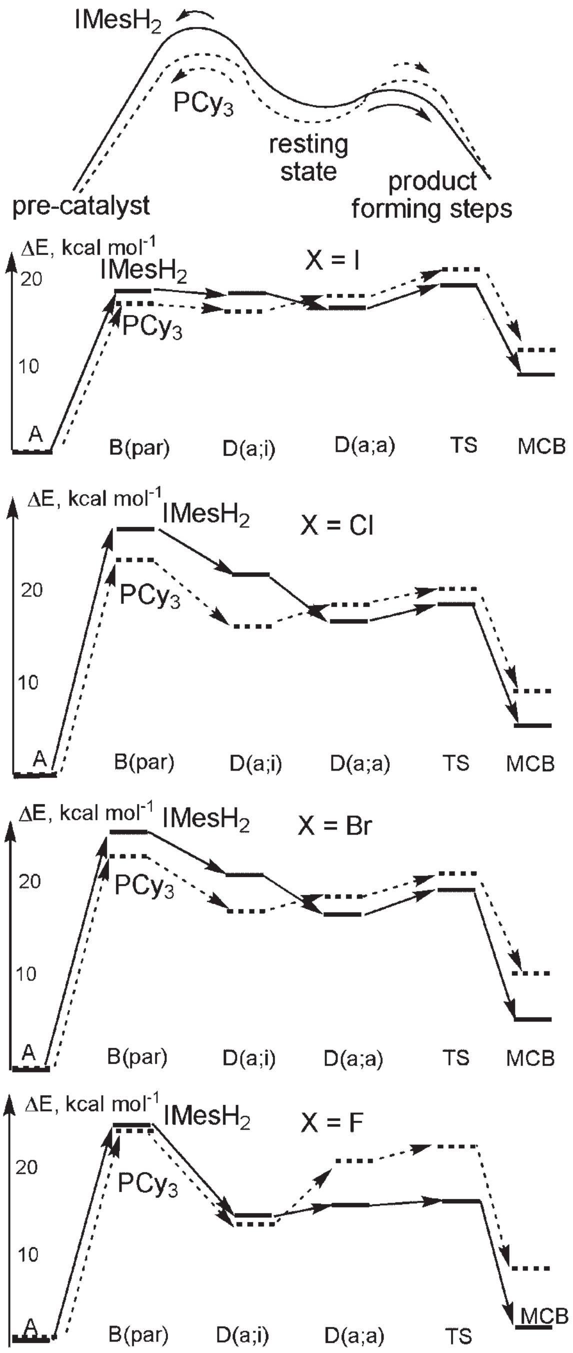

Figure 5. Most favorable reaction pathways of MCB formation in 1st-generation (dashed line) and 2nd-generation Grubbs catalysts

more effective formation of the active D(a;a) complex. A surprisingly low barrier for conversion of the active D(a;a) complex into the MCB was calculated for the 2nd-generation Grubbs catalysts with X = F, which should lead to the most active catalyst. Unfortunately, these data cannot be supported by experiment, since no data are available so far. On the basis of existing correlations between the relative stability of the two conformers of the 14-electron intermediates and barriers for transformation of active D(a;a) complex into the MCB, it can be supposed that further improvement of the catalytic activity of 2nd-generation Grubbs catalysts may be achieved by use of an L ligand that causes the strong stabilization of the orthogonal conformer B(ort).

SUMMARY

Systematic comparative quantum chemical calculations on the reaction pathway of MCB formation with NBE for 1st- and 2nd-generation Grubbs catalysts in dependence on the ligand X = I, Br, Cl, and F have been carried out and shown that the mechanism suggested by Straub can in fact be applied to the reaction cascade necessary for the ROMP of NBE. Important findings are that: (i) the active D(a;a) complex is energetically more stable than the inactive D(a;i) complex in the case of 2nd-generation Grubbs catalysts, (ii) in agreement with experiment, the possible rate limiting barriers for the conversion of the π-complex into the corresponding MCB are systematically larger in the case of 1st-generation Grubbs catalysts due to a necessary additional re-arrangement for the formation of the active D(a;a) complex from the more stable inactive D(a;i) one. Not unexpected, there is a strong influence of both the L and X ligands on conformational properties and the relative stabilities of the 14-electron intermediates, which has a direct effect on the distribution of the inactive and active conformations of NBE–carbene intermediates. In case of 2nd-generation Grubbs catalysts, the more effective formation of the active D(a;a) complex from the 14-electron intermediate may be explained by the more effective stabilization of the active orthogonal conformation of the carbene unit by the $IMesH_2$ ligand. Finally, there is a clear correlation between the conformational properties of the 14-electron intermediate and the relative stability of the active D(a;a) complex, which is the most important structure for the conversion of the π-complex into the MCB. Thus, the smaller the energy difference between the more stable B(par) and the less stable the B(ort) conformer of the 14-electron intermediate, the more stable is the active D(a;a) complex. The calculated data fit well with the experimental ones.

SUPPLEMENTARY INFORMATION AVAILABLE:

The structures of studied complexes.

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