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Theoretical studies of ethylene addition to transition metal compounds with carbene and oxo groups $L_nM(=CH_2)(=O)$[†,‡]

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ABSTRACT: Quantum chemical calculations using density functional theory at the B3LYP level in combination with relativistic effective core potentials for the metals and TZ2P valence basis sets have been carried out for elucidating the reaction pathways of ethylene addition to $MeReO_2(CH_2)$ (**C1**). The results are compared with our previous studies of ethylene addition to $OsO_2(CH_2)_2$ (**A1**) and $OsO_3(CH_2)$ (**B1**). Significant differences have been found between the ethylene additions to the osmium compounds **A1** and **B1** and the rhenium compound **C1**. Seven pathways for the reaction **C1**+C_2H_4 were studied, but only the $[2+2]_{Re,C}$ addition yielding rhenacyclobutane **C5** is an exothermic process with a high activation barrier of 48.9 kcal mol^{-1}. The lowest activation energy (27.7 kcal mol^{-1}) is calculated for the $[2+2]_{Re,C}$ addition, which leads to the isomeric form **C5′**. Two further concerted reactions $[3+2]_{O,C}$, $[3+2]_{O,O}$, and $[2+2]_{Re,O}$ and the addition/hydrogen migration of ethylene to one oxo ligand are endothermic processes which have rather high activation barriers (>35 kcal mol^{-1}). Four isomerization processes of **C1** have very large activation energies of >65 kcal mol^{-1}. The ethylene addition to the osmium compounds **A1** and **B1** are much more exothermic and have lower activation barriers than the C_2H_4 addition to **C1**. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: Density Functional Theory; oxo ligands; carbene ligands; reaction mechanism; transition metal complexes

INTRODUCTION

Quantum chemical studies have shown that the initial step of the *cis*-dihydroxylation of olefins with OsO_4 is a concerted [3+2] addition yielding an osma-2,5-dioxolane as reaction product.[1] The alternative two-step reaction pathway with initial [2+2] addition followed by rearrangement of the osmaoxetane has much higher activation barriers. This finding is now undisputed in the community. Further theoretical work predicted that the reaction of RuO_4 with olefins also starts with a concerted [3+2] addition.[2] These predictions were recently corroborated in experimental investigations, which showed that ruthenium compounds containing a $Ru(=O)_2$ group react with olefins in the expected [3+2] fashion to yield ruthena-2,5-dioxolanes as reaction products.[3] Much less is known about the reaction of olefins with transition metal compounds, which carry doubly bonded ligands X other than oxygen in $L_nM(=O)(=X)$.

Deubel and Muñiz reported theoretical studies on the reaction pathways of the addition of $OsO_2(NH)_2$ to ethylene.[4] These calculations predict that the three possible [3+2] addition reactions are kinetically and thermodynamically favored over the two alternative [2+2] additions, and that the diamination should be the most favorable reaction. A substantially more complicated scenario was found in our recent theoretical study on the addition of C_2H_4 to $OsO_2(CH_2)_2$.[5] Besides the energetically favored [3+2] additions, we found addition reactions with coupled hydrogen migration as well as isomerization of $OsO_2(CH_2)_2$ to metallacyclic species, which open up numerous reaction pathways. Subsequent calculations on the reaction pathways for addition of C_2H_4 to $OsO_3(CH_2)$ revealed a related, but somewhat

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different picture.[6] In the meantime, we theoretically investigated the addition of ethylene to $MeReO_2(CH_2)$, which exhibits yet another reaction profile. The corresponding reactivity of this compound is particularly interesting because substituted derivatives RCH_2ReO_2 (CHR) have been synthesized by Schrock.[7] The reaction of the latter with R = *t*-Bu with olefins has been investigated in a study on transition metal metathesis reactions,[8] but without further information the authors stated that the compound shows no metathesis reactivity. The molecule $MeReO_2(CH_2)$ is thus a model compound for an experimentally known species while oxo-carbene complexes $L_nM(=O)(=X)$ of osmium to the best of our knowledge have not been synthesized so far. A recent review by Schrock indicates that only 10 compounds of the general formula $L_nM(=O)(=X)$ have been isolated.[7] The metal atom in the oxo-carbene complexes is tungsten, rhenium, or molybdenum.

In this paper, we compare the theoretical results of the reaction courses for the addition of C_2H_4 to $OsO_2(CH_2)_2$[5], $OsO_3(CH_2)$[6] which were recently published with calculated data for the addition reaction to $MeReO_2(CH_2)$. For the reaction $C_2H_4+OsO_2(CH_2)_2$, we will report further data which have been obtained after publication of references 5 and 6. Please note that the calculated energies given in reference 6 have been obtained using the smaller basis set B3LYP/I (see below for theoretical details). Therefore the data given there are slightly different from the values reported here. Some energetically unfavorable reaction steps reported in references 5 and 6 are omitted because they are not relevant for the comparison with the rhenium system. The results for $MeReO_2(CH_2)$ have not been reported so far. The theoretical findings exhibit a fascinating variety of reaction pathways, which constitute a challenge for experimental studies. We want to emphasize that the results presented here are still far away from a complete coverage of the possible reaction pathways for the three reactions discussed. Further efforts, both theoretical and experimental, are needed to unravel the reaction course for olefin addition to oxo carbene complexes.

COMPUTATIONAL METHODS

The calculations have been performed at the density functional theory (DFT) level employing the B3LYP hybrid functional[9] as implemented[10] in the Gaussian 03 program.[11] The TZVP all electron basis set of Ahlrichs and coworkers was employed for C, O, and H.[12] For Os and Re, the Stuttgart/Köln relativistic effective core potential replacing 60 core electrons was used in combination with a (311111/22111/411) valence basis.[13] This combination is denoted here as basis set I. All minima and transition structures were optimized at this level of theory without symmetry constraints. Analytic Hessians computed at B3LYP/I were used to characterize the nature of stationary points and to obtain (unscaled) zero-point vibrational energy contributions (ZPE). All connectivities of minima and transition structures were verified by intrinsic reaction coordinate (IRC)[14] following calculations at this level of theory. Based on the B3LYP/I geometries, additional single point calculations were performed employing the larger basis set II, in which the Stuttgart/Köln valence basis sets for Os and Re were augmented by two sets of f-functions and one set of g-functions derived by Martin and Sundermann[15] and used in combination with the correlation consistent cc-pVTZ basis set of Dunning[16] for C, O, and H atoms. All relative energies discussed below relate to B3LYP/II//B3LYP/I calculations and include ZPE contributions.

RESULTS AND DISCUSSION

Let us first introduce the notation used throughout this paper for the compounds studied: Molecules of the system $C_2H_4+OsO_2(CH_2)_2$ carry the prefix **A**, whereas the prefix **B** is used for the system $C_2H_4+OsO_3(CH_2)$ and **C** for $C_2H_4+MeReO_2(CH_2)$. The same numbering scheme is employed for related structures of all three systems in order to facilitate the comparison.

Figure 1 shows the calculated reaction profile for the addition of C_2H_4 to $OsO_2(CH_2)_2$ (**A1**). Three different [3+2] pathways yield the respective metallacycles **A2**, **A3**, and **A4**. The kinetically most favorable reaction is the $[3+2]_{O,C}$ addition **A1**+$C_2H_4 \rightarrow$ **A3** with an activation barrier of only 8.1 kcal mol^{-1}. The reaction is exothermic by −42.4 kcal mol^{-1}. However, **A3** is not the most stable reaction product of the three [3+2] additions. The kinetically next favorably reaction is the $[3+2]_{C,C}$ addition **A1**+$C_2H_4 \rightarrow$ **A2** which has a higher activation barrier of 13.0 kcal mol^{-1}, but it is exothermic by −72.7 kcal mol^{-1}. The calculations thus predict that the outcome of the [3+2] addition of C_2H_4 to $OsO_2(CH_2)_2$ depends on the kinetic and thermodynamic control of the reaction conditions. The third concerted pathway is the $[3+2]_{O,O}$ addition **A1**+$C_2H_4 \rightarrow$ **A4**, which has a clearly higher activation barrier of 27.5 kcal mol^{-1}. The latter reaction is only slightly exothermic by −7.0 kcal mol^{-1} and this process can thus not compete with the other [3+2] additions. Moreover, there are two other reactions more favorable than the $[3+2]_{O,O}$ addition. The ethylene molecule may add to one of the oxygen atoms with concurrent hydrogen migration either from ethylene to a methylene ligand **A1**+$C_2H_4 \rightarrow$ **A7** or from a methylene group to ethylene **A1**+$C_2H_4 \rightarrow$ **A8** (Fig. 1). Both reactions are exothermic by −30.4 kcal mol^{-1} (**A1**+$C_2H_4 \rightarrow$ **A7**) and by −12.6 kcal mol^{-1} (**A1**+$C_2H_4 \rightarrow$ **A8**). Although the former reaction is more exothermic, it has a higher activation barrier (27.6 kcal mol^{-1}) than the latter (21.2 kcal mol^{-1}). Both reactions are clearly less favorable than the $[3+2]_{C,C}$ and $[3+2]_{O,C}$ additions. Please note that the reaction **A1**+$C_2H_4 \rightarrow$ **A7**

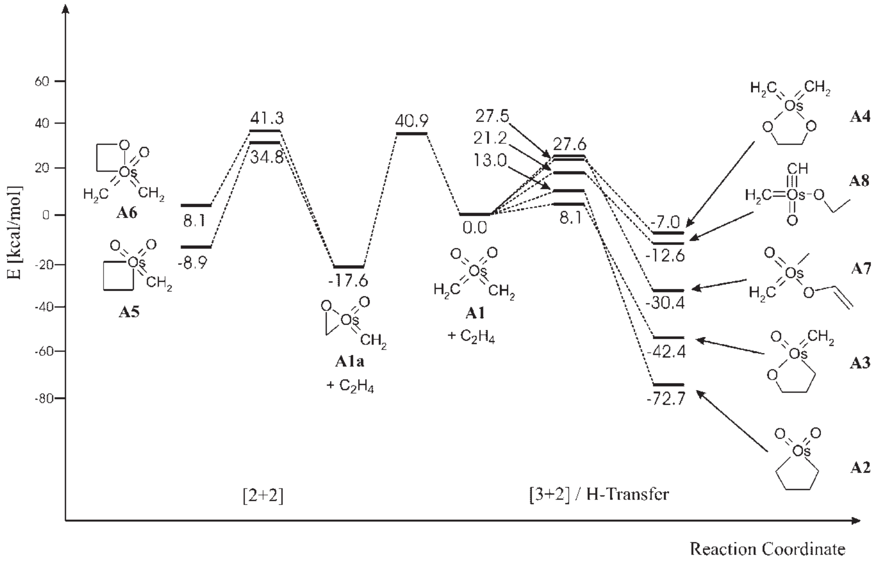


Figure 1. Calculated reaction profile at B3LYP/II//B3LYP/I+ZPE for the addition of C_2H_4 to $OsO_2(CH_2)_2$ (**A1**)

was not reported in reference 5. The reaction step was only found after the paper was published.

What about the [2+2] addition reactions of C_2H_4 to $OsO_2(CH_2)_2$? All attempts to identify such a reaction path for the parent molecule **A1** failed. We did find transition states whose visual inspection gave the false impression that they belong to the $[2+2]_{Os,O}$ and $[2+2]_{Os,C}$ pathways of the C_2H_4+**A1** reaction. IRC calculations revealed, however, that the energy minimum connected to the transition states is not **A1** but the osmaoxirane isomer **A1a**, which is 17.6 kcal mol^{-1} more stable than **A1**. The activation barrier for the isomerization **A1** → **A1a** is very high (40.9 kcal mol^{-1}). The $[2+2]_{Os,C}$ addition **A1a**+C_2H_4 → **A5** and the $[2+2]_{Os,O}$ reaction **A1a**+ C_2H_4 → **A6** are also kinetically unfavorable. The activation barriers with respect to **A1a** are 52.4 kcal mol^{-1} for the former reaction and 58.9 kcal mol^{-1} for the latter. Both reaction steps are endothermic by 8.7 kcal mol^{-1} ($[2+2]_{Os,C}$) and 25.7 kcal mol^{-1} ($[2+2]_{Os,O}$). Note that the osmaoxirane ring opens up during the reaction course.

The data given in Fig. 1 indicate that the most likely thermal reactions of **A1** with C_2H_4 are the [3+2] additions yielding **A2** and **A3**. All other reactions are kinetically and thermodynamically much less likely to occur. The ring closure **A1** → **A1a** should also not take place because the activation barrier is too high. However, there is one more reaction of **A1** that might compete with the $[3+2]_{C,C}$ and $[3+2]_{O,C}$ additions, that is, the isomerization via C—C coupling **A1** → **A1b** shown in Fig. 2. The activation barrier is only 15.7 kcal mol^{-1} and the reaction is strongly exothermic by −56.2 kcal mol^{-1}. But the isomer **A1b** is not very reactive toward addition of ethylene. The $[3+2]_{O,O}$ reaction **A1b** → **A9** and the $[2+2]_{Os,O}$ reaction **A1b** → **A10** have very high barriers of > 50 kcal mol^{-1}. Both reaction steps are endothermic. In the presence of further oxidant it is possible, however, that the formation of **A1b** opens up further reaction pathways such as oxidation to the Os(VIII) species O_3Os(*cyc*-C_2H_4). Finally we want to mention that the ring closure of **A1** through O—O coupling yielding a bisalkylideneosmaperoxide species is a strongly endothermic process by 64.6 kcal mol^{-1}, which has a prohibitively high activation barrier of 88.5 kcal mol^{-1}.[5] This process is, therefore, not considered further in the following.

The most important reaction pathways for addition of ethylene to the monocarbene $OsO_3(CH_2)$ **B1** are shown in Fig. 3. A Comparison with Fig. 1 reveals several significant differences between the reactions **A1**+C_2H_4 and **B1**+C_2H_4. Only two [3+2] additions with C_2H_4 are possible for the monocarbene **B1**. The $[3+2]_{O,C}$ reaction **B1**+C_2H_4 → **B3** and the $[3+2]_{O,O}$ reaction **B1**+C_2H_4 → **B4** are slightly more exothermic and have lower activation barriers than the respective [3+2] reactions of **A1**. Note that the $[3+2]_{O,O}$ reaction of **B1** has a significantly lower barrier (11.8 kcal mol^{-1}) than the $[3+2]_{O,O}$ reaction of **A1** (27.5 kcal mol^{-1}). A similar correlation is found for the comparison between the addition reactions of ethylene to the oxo group with simultaneous hydrogen migration yielding **B7** and **B8** with the reactions of **A1**, except that the formation of **B8** is slightly less exothermic than the reaction **A1**+C_2H_4 → **A8**.

A major difference between the two systems **A** and **B** is the finding that in the latter, there is a transition state for the $[2+2]_{Os,O}$ addition reaction **B1**+C_2H_4 → **B6**, which could not be found for **A1**. This reaction has a rather high activation barrier of 36.2 kcal mol^{-1} and is slightly endothermic by 9.6 kcal mol^{-1} It is thus clearly unfavorable compared to the [3+2] addition reactions and to the addition of ethylene to oxygen with concurrent hydrogen migration. The isomerization through C—O bond formation **B1** → **B1a** has a slightly higher barrier (41.3 kcal mol^{-1}) but is more exothermic (−27.5 kcal mol^{-1}) than the related process **A1** → **A1a**.

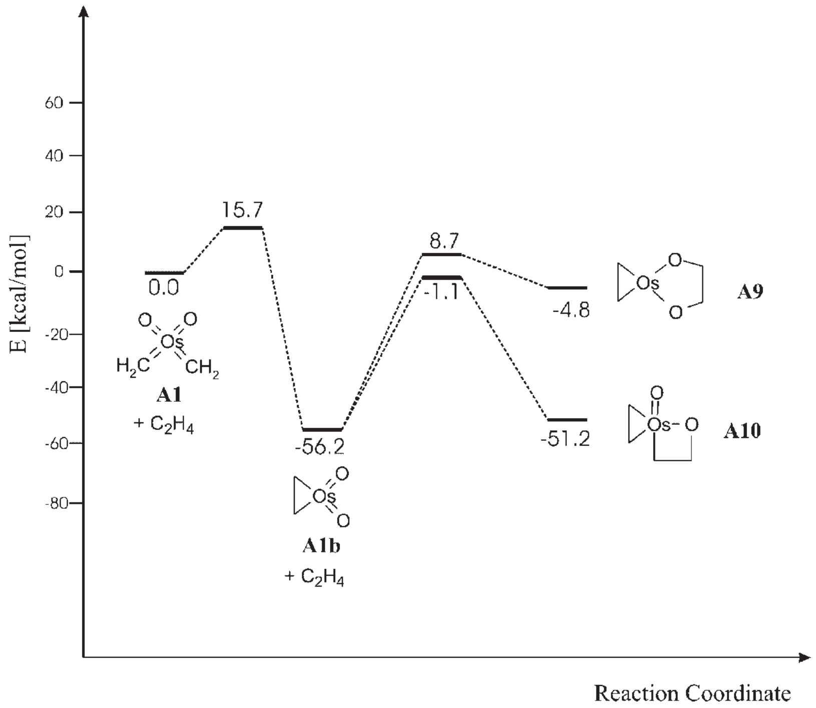


Figure 2. Calculated reaction profile at B3LYP/II//B3LYP/I+ZPE for the addition of C_2H_4 to $OsO_2(CH_2)_2$ (**A1b**)

Figure 3 shows that the osmaoxetane species **B6** may also be formed through $[2+2]_{Os,O}$ ethylene addition to **B1a**. The latter process **B1a**+$C_2H_4 \rightarrow$ **B6** has a slightly lower barrier with respect to **1** (34.9 kcal mol^{-1}) than the reaction **B1**+$C_2H_4 \rightarrow$ **B6** (36.2 kcal mol^{-1}). However, the former reaction is energetically less favorable because it requires the prior isomerization reaction **B1** $\rightarrow$ **B1a** which has an activation energy of 41.3 kcal mol^{-1}. It is interesting to note that there are two distinctively different reaction pathways starting from **B1** which lead to the formation of **B6**. Rather unusual and surprising results were found for the ethylene addition across the Os═C bond yielding osmacyclobutane as reaction product. Two different pathways for the $[2+2]_{Os,C}$ ethylene addition to **B1** leading to two different isomers **B5** and **B5′** could be identified via IRC calculations starting from the respective transition states of **B1**+$C_2H_4 \rightarrow$**B5** and **B1**+$C_2H_4 \rightarrow$**B5′**. They were found

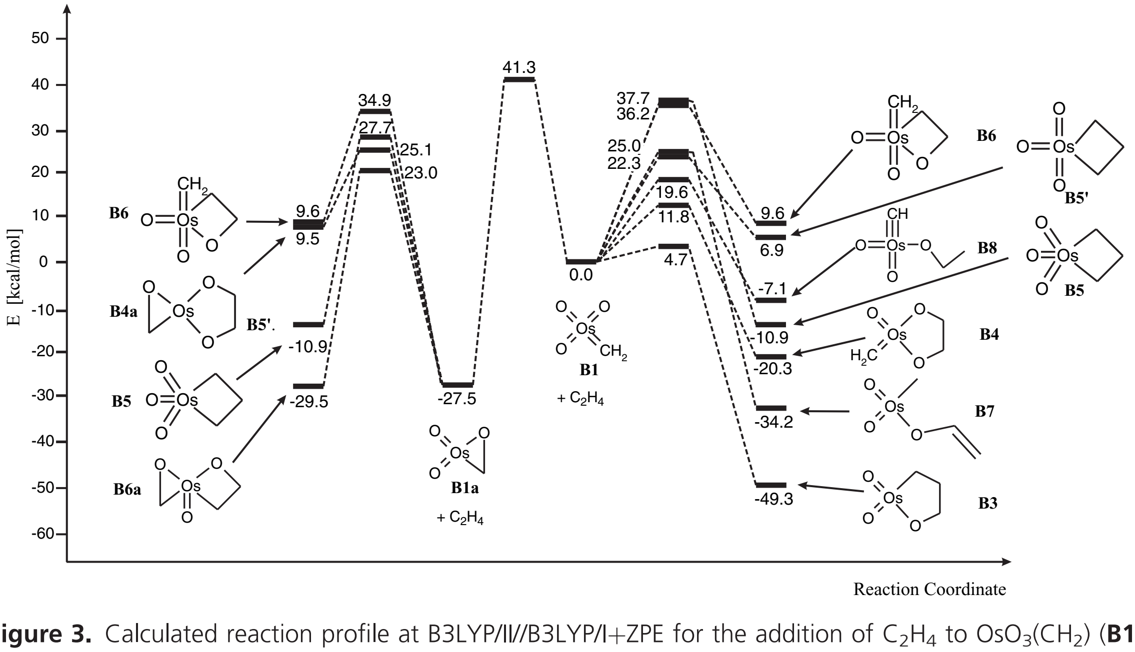


Figure 3. Calculated reaction profile at B3LYP/II//B3LYP/I+ZPE for the addition of C_2H_4 to $OsO_3(CH_2)$ (**B1**)

after reference 6 was published and therefore, they are not shown there. Figure 3 shows that the $[2+2]_{Os,C}$ addition is kinetically and thermodynamically more favorable than the $[2+2]_{Os,O}$ addition but it is clearly less favorable than the $[3+2]_{O,C}$ and $[3+2]_{O,O}$ addition reactions. The most surprising finding is that the exothermic formation of the more stable isomer **B5** has a significantly larger activation barrier (37.7 kcal mol^{-1}) than the endothermic addition reaction which leads to the less stable isomer **B5′**. The activation energy for the latter reaction is only 22.3 kcal mol^{-1}. The geometries of the transition states for the $[2+2]_{Os,C}$ addition reactions and optimized structures of the osmacylobutanes **B5** and **B5′** are shown below in Figure 5. They will be discussed in conjunction with the related rhenium system for which a similar situation was found. The osmacyclobutane species **B5** may also be formed via $[2+2]_{Os,C}$ ethylene addition to **B1a**. Since the latter process requires the prior isomerization reaction **B1**→**B1a** which has an activation energy of 41.3 kcal mol^{-1} the reaction is less favored than the direct $[2+2]_{Os,C}$ ethylene addition to **B1**. Like for the $[2+2]_{Os,O}$ addition yielding **B6** there are two distinctively different reaction pathways starting from **B1** which lead to the formation of **B5**.

Two transition states for addition reactions of ethylene to **B1a** where the metallaoxirane ring remains intact have been identified which could not be found for the reaction of C_2H_4 with **A1a**. These are the $[3+2]_{O,O}$ addition **B1a**+C_2H_4 → **B4a** and the $[2+2]_{Os,O}$ addition **B1a**+ C_2H_4 → **B6a**. The compounds **B4a** and **B6a** are isomers of **B4** and **B6**, respectively, which contain an osmaoxirane moiety. **B6a** is 39.1 kcal mol^{-1} lower in energy than **B6** (Fig. 3). The osmaoxirane formation **B6** → **B6a** is thus even more exothermic than the isomerization **B1** → **B1a**, which proceeds −27.5 kcal mol^{-1} downhill. But formation of an osmaoxirane moiety from an oxo and an alkylidene group is not always an exothermic process. In particular, the isomerization **B4** → **B4a** is endothermic by 29.8 kcal mol^{-1}. This may be explained with the change in the formal oxidation state during the processes. There is a change from Os(VIII) to Os(VI) in the reactions **B1** → **B1a** and **B6** → **B6a** while the oxidation state changes from Os(VI) to Os(IV) during the reaction **B4** → **B4a**. In our previous study on the oxidation of ethylene to OsO_4 and RuO_4, we found that the reaction energies strongly depend on the change of the oxidation state.[2]

The data in Fig. 3 thus show that, like in system **A**, the kinetically most favorable reactions of **B1** with ethylene are [3+2] additions yielding the compounds **B3** and **B4**. The reaction **B1**+C_2H_4 → **B7** is thermodynamically more favorable than the formation of **B4** but the latter process has a lower activation energy. All other addition reactions and the ring closure **B1** → **B1a** should not take place because the activation energies are too high.

The calculated reaction profile for ethylene addition to $MeReO_2(CH_2)$ (**C1**) which is shown in Fig. 4 exhibits substantial differences compared to the addition reactions of **A1** and **B1**. The most important difference concerns the $[3+2]_{O,C}$ and $[3+2]_{O,O}$ additions to **C1** yielding **C3** and **C4** which are calculated to be *endo*thermic reactions for the rhenium system with rather high activation barriers of 35.7 kcal/mol and 63.9 kcal/mol, respectively. The corresponding reactions of the osmium system were strongly *exo*thermic. Like for the osmium compound **B1**, two transition states for the $[2+2]_{Re,C}$ reactions **C1**+C_2H_4→**C5** and **C1**+C_2H_4→**C5′** were found on the PES. The former process is the *only* exothermic addition reaction of **C1** but it has a rather high activation barrier of 48.9 kcal mol^{-1}. The addition reaction yielding

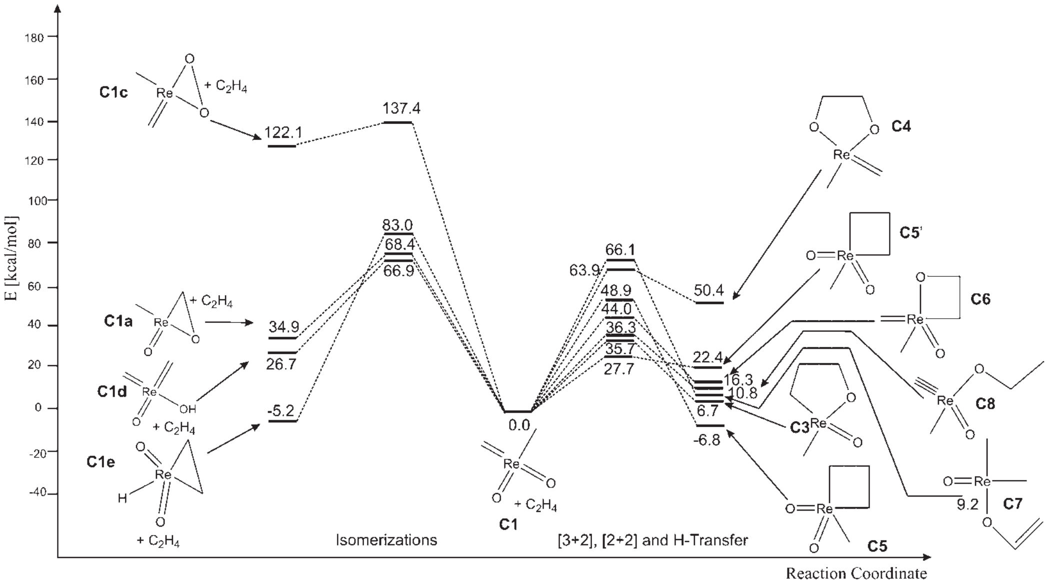
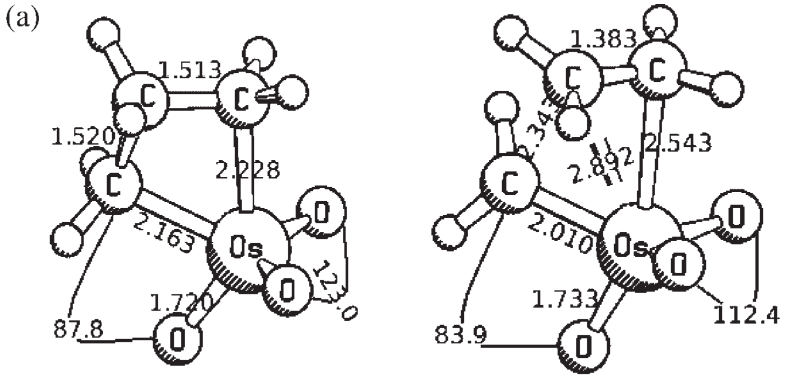
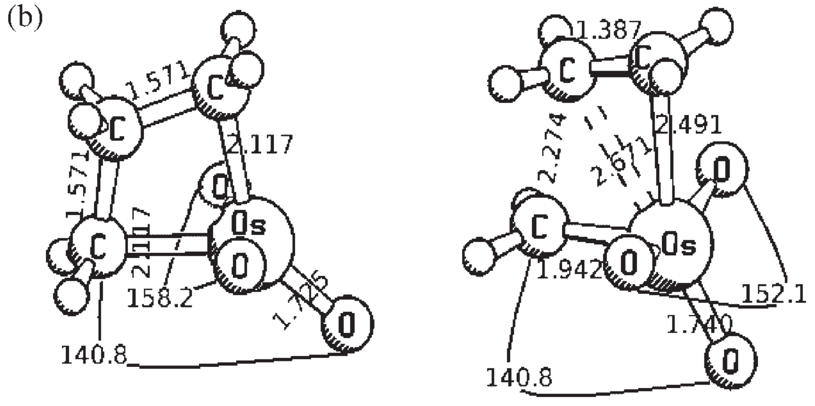


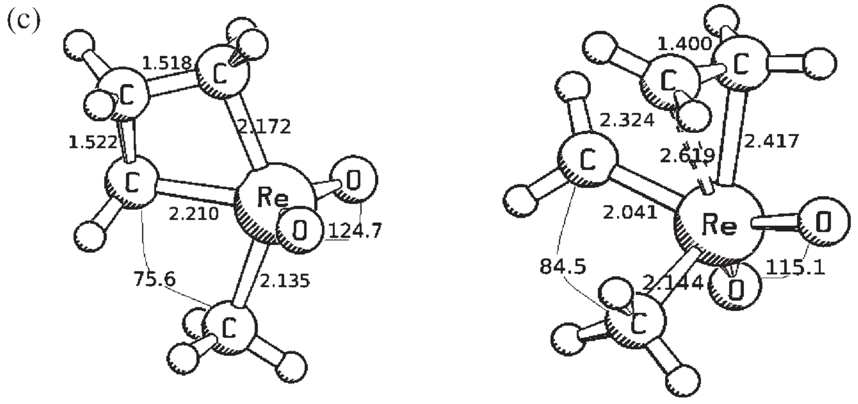
Figure 4. Calculated reaction profile at B3LYP/II//B3LYP/I+ZPE for the addition of C_2H_4 to $MeReO_2(CH_2)$ (**C1**)



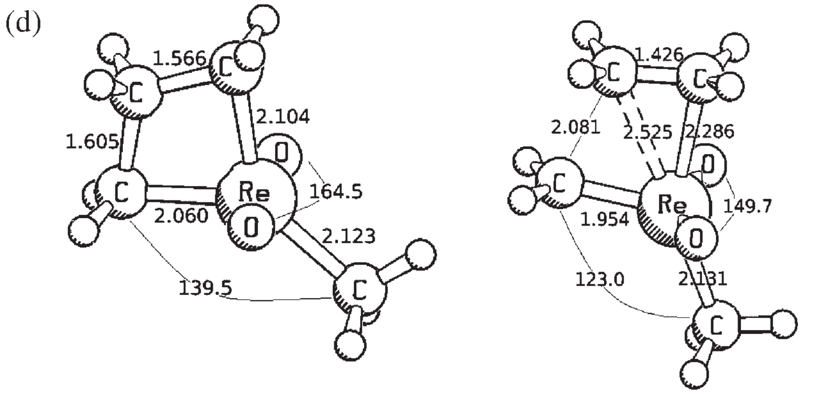
B5 TS(**B1** + C_2H_4 → **B5**)



B5' TS(**B1** + C_2H_4 → **B5'**)



C5 TS(**C1** + C_2H_4 → **C5**)



C5' TS(**C1** + C_2H_4 → **C5'**)

the rhenacyclobutane species **C5′** is endothermic by 22.4 kcal/mol higher in energy (Fig. 4). However, the activation energy for the formation of the higher energy form C5′ is again much lower (27.7 kcal/mol) than the reaction **C1**+C_2H_4→**C5**. The calculations thus predict (Figure 4) that the kinetically most favorable process is the $[2+2]_{Re,C}$ reaction yielding the high-energy isomer **C5′** while the $[2+2]_{Re,C}$ reaction yielding the low-energy isomer **C5** is the thermodynamically most favorable process. The $[2+2]_{Re,O}$ reaction **C1**+C_2H_4→**C3** is endothermic and it has a rather high activation barrier of 44.0 kcal/mol. The addition of ethylene to oxygen atom with simultaneous hydrogen migration **C1**+C_2H_4→**C7** which was exothermic for the osmium system is for the rhenium compound an endothermic process by 9.2 kcal/mol which has a large barrier of 66.1 kcal/mol. Finally, the addition of ethylene with simultaneous hydrogen migration **C1**+C_2H_4→**C8** is another endothermic process by 10.8 kcal/mol which has a sizeable barrier of 35.7 kcal/mol.

Figure 4 shows also four isomerization reactions of **C1**. The C—O and O—O ring closure processes **C1** → **C1a** and **C1** → **C1c** are endothermic reactions with high activation barriers. The 1,3-hydrogen migration **C1** → **C1d** is also energetically unfavorable, both kinetically and thermodynamically. The C—C ring closure reaction with simultaneous hydrogen migration **C1** → **C1e** is slightly exothermic, but the activation barrier of 83.0 kcal mol^{-1} is prohibitively high. The calculations thus predict that compound **C1** is not very reactive towards ethylene addition.

The peculiar energetic ordering of the isomeric forms of the osmium system **B5** and **B5′** and the rhenium system **C5** and **C5′** on the one hand and the respective transition states for the former system TS(**B1**+C_2H_4→**B5**) and TS(**B1**+C_2H_4→**B5′**) and for rhenium TS(**C1**+C_2H_4→**C5**) and TS(**C1**+C_2H_4→**C5′**) on the other hand attracted our attention. The optimized structures are shown in Figure 5. The low-energy forms **B5** and **C5** have a trigonal bipyramidal structure while the high-energy isomers **B5′** and **C5′** are distorted square pyramids. Experimental evidence shows that the energetically most favorable geometry for pentacordinated Os(VIII) and Re(VII) compounds is a trigonal bipyramide.[17] This explains why **B5′** and **C5′** are higher in energy than **B5** and **C5**, respectively. The search for a transition state for interconversion between **C5** and **C5′** was not successful. This can be explained by the finding that the transition state for ethylene addition to **C5′** is only 5.5 kcal mol^{-1} higher in energy than the separated molecules. A rather small distortion of the structure of **C5′** leads during the geometry optimization to dissociation of C_2H_4 rather than to structure **C5**. We could also not yet find a transition state for the for interconversion between **B5** and **B5′**. Closer inspection of the transition states of the osmium system TS(**B1**+C_2H_4→**B5**) and TS(**B1**+C_2H_4→**B5′**) and for the rhenium system TS(**C1**+C_2H_4→**C5**) and TS(**C1**+C_2H_4→**C5′**) (Figure 5) shows an in-plane approach of the ethylene to the H_2C-Os-O_{trans} and H_2C-Re-CH_3 moieties in the transition states for formation of the less stable forms **B5′** and **C5′** which comes close to a least-motion pathway. In the higher-lying transition states TS(**B1**+C_2H_4→**B5**) and TS(**C1**+C_2H_4→**C5**) the C_2H_4 molecule attacks **B1** and **C1** from a direction where it must subsequently rotate about the M-(CH_2CH_2) (M=Os, Re) axis in order to achieve the C-C ring coupling. The significant deviation of the latter reactions suggests that it is a symmetry forbidden reaction, which explains the much higher activation barriers than for the former processes.

SUMMARY

The results of this work can be summarized as follows. The calculated reaction coordinates for ethylene addition to $OsO_2(CH_2)_2$ (**A1**), $OsO_3(CH_2)$ (**B1**), and $MeReO_2(CH_2)$ (**C1**) exhibit significant differences among the activation energies and reaction energies of the three systems. Seven reaction courses for the reaction **C1**+C_2H_4 were found in this study, but only the $[2+2]_{Re,C}$ addition yielding rhenacyclobutane **C5** is an exothermic process. The reaction has a high activation barrier of 48.9 kcal mol^{-1}. The lowest activation energy (27.7 kcal mol^{-1}) is calculated for the $[2+2]_{Re,C}$ addition which leads to the isomeric form **C5′**. Three further concerted reactions $[3+2]_{O,C}$, $[3+2]_{O,O}$, and $[2+2]_{Re,O}$ and two addition reactions of ethylene to one oxo ligand with simultaneous hydrogen migration are endothermic processes which have rather high activation barriers (>35 kcal mol^{-1}). Four isomerization processes of **C1** have very large activation energies of >65 kcal mol^{-1}).

In contrast to the ethylene addition to the rhenium system **C1**, the addition reactions to the osmium compounds **A1** and **B1** are much more exothermic and they have lower barriers, particularly for the [3+2] reactions. Five reaction courses were found for **A1**+C_2H_4.[5] The lowest activation barrier is calculated for the $[3+2]_{O,C}$ addition followed by the $[3+2]_{C,C}$

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Figure 5. Optimized structures at B3LYP/II//B3LYP/I of the isomeric forms of the metallacyclobutanes of osmium **B5** and **B5′** and rhenium **C5** and **C5′** and for the corresponding transition states. (a) Osmacyclobutane **B5** and transition state TS(**B1**+C_2H_4→**B5**); (b) Osmacyclobutane →**B5′** and transition state TS(**B1**+C_2H_4→**B5′**); (c) Rhenacyclobutane **C5** and transition state TS(**C1**+C_2H_4→**C5**); (d) Rhenacyclobutane **C5′** and transition state TS(**C1**+C_2H_4→**C5′**); Interatomic distances in Å, angles in degree

pathway which is thermodynamically more favorable than the former process. Both reactions are strongly exothermic and have activation barriers <15 kcal mol^{-1}. The $[3+2]_{O,O}$ addition of **A1** and two addition reactions to one oxygen atom of **A1** with simultaneous hydrogen migration onto or from the ethylene molecule have higher activation barriers and are clearly less exothermic than the former processes. The [2+2] additions of ethylene across the Os═O and Os═CH_2 bonds take only place after initial isomerization of **A1** to the osmaoxirane species **A1a**. The rearrangement **A1**→**A1a** and the $[2+2]_{Os,O}$ and $[2+2]_{Os,C}$ additions to the latter have very high activation barriers (>40 kcal mol^{-1}). A low activation barrier of 15.7 kcal mol^{-1} is predicted for the isomerization of **A1** via C—C coupling to the osmacyclopropane species **A1b** which, however, has very high activation barriers for the [2+2] and [3+2] addition of ethylene (>55 kcal mol^{-1}).

Five reaction courses were found in our earlier study for the system **B1**+C_2H_4[6] while two more reactions pathways could be identified during this work. The exothermic $[3+2]_{O,C}$ and $[3+2]_{O,O}$ addition reactions have the lowest activation barriers (<12 kcal mol^{-1}). Two pathways for ethylene addition to one oxo ligand with concurrent hydrogen migration have higher barriers although one of them is more exothermic than the $[3+2]_{O,O}$ addition. Unlike **A1**, a transition state for $[2+2]_{Os,O}$ addition of ethylene to **B1** was found which is high in energy (36.2 kcal mol^{-1}). Like for the rhenium system **C1**, the $[2+2]_{Os,C}$ addition to **B1** may proceed via two different transition states yielding to metallacyclubutane isomers **B5** and **B5′**. The formation of the significantly less stable form **B5′** requires less activation energy than the reaction yielding the more stable isomer **B5**. A high barrier of 41.3 kcal mol^{-1} is also calculated for the isomerization of **B1** to the osmaoxirane **B1a**. The activation energies for the [2+2] and [3+2] reactions **B1a**+C_2H_4 are very large (>50 kcal mol^{-1}).

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