



## Computational studies of the mechanistic aspects of olefin metathesis reactions involving metal oxo-alkylidene complexes

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### ARTICLE INFO

#### Article history:

Received 19 April 2011

Received in revised form 24 May 2011

Accepted 25 May 2011

Available online 22 June 2011

#### Keywords:

Metathesis

Catalyst

Oxo-alkylidene

Metallacyclobutane

Mechanism

Density functional theory

### ABSTRACT

The reactions of  $\text{Cl}_2(\text{O})\text{MCH}_2$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}, \text{Ru}, \text{Re}$ ) with ethylene, models of potential chain-carrying catalysts and olefins respectively in the metal-catalyzed olefin reaction, have been studied using hybrid density functional theory at the B3LYP/LACVP\* and MO6/LACVP\* levels of theory. It was found that formation of the metallacyclobutane, a key intermediate in the olefin metathesis reaction according to the Herrison–Chauvin mechanism, is a low-barrier process for each of the complexes studied, the highest barrier occurring in Ru (13.78 kcal/mol by B3LYP calculations and 4.74 kcal/mol by MO6 calculations) and the lowest barrier occurring in W (0.38 kcal/mol by B3LYP and 0.28 kcal/mol by MO6). However, for  $\text{M} = \text{Cr}$  the [3+2] addition of the olefinic bond of ethylene across the Cr–O and Cr–C bonds of the complex has a lower activation barrier than the metallacyclobutane formation step,  $\text{Cl}_2(\text{O})\text{CrCH}_2$  may not promote olefin metathesis. Also, for  $\text{M} = \text{Ru}$  the activation barrier of the [3+2] addition of ethylene across the Ru–O and Ru–Cl bonds is 3.61 kcal/mol lower than the barrier of the metallacyclobutane formation step, at the B3LYP level of theory, suggesting that  $\text{Cl}_2(\text{O})\text{RuCH}_2$  may not promote olefin metathesis. However, the MO6 results indicate that the barrier for metallacyclobutane formation is 3.55 kcal/mol lower than that for the [3+2] addition across the Ru–O and Ru–Cl bonds, suggesting that  $\text{Cl}_2(\text{O})\text{RuCH}_2$  may catalyze metathesis. At either level of theory, the difference in activation barriers between the productive [2+2] route and the [3+2] route is not high enough to preclude either pathway from manifesting. Thus, metallacyclobutane formation may occur in the Ru complex, albeit very unselectively. However, the metallacyclobutane intermediate formed is very stable (31.45 kcal/mol and 42.57 kcal/mol by B3LYP and MO6 respectively) and may not easily undergo cycloreversion to form the final product, i.e. a dead end in the catalytic cycle. For  $\text{M} = \text{Mo}, \text{W}$ , and  $\text{Re}$ , the metallacyclobutane formation pathway is more favorable than the potential side reactions, the differences between the productive [2+2] pathway and the lowest-barrier side reactions being 19.30, 25.87, 3.54 kcal/mol respectively at the B3LYP level and 13.82, 18.81 and 4.06 kcal/mol respectively at the MO6 level. Thus, the selectivity of the metallacyclobutane formation, which is marginal in  $\text{Re}$ , is in the order:  $\text{W} > \text{Mo} > \text{Re}$ . However, the metallacyclobutane formed in  $\text{Re}$  may be too stable to allow cycloreversion to form the final product. Thus metathesis is predicted to occur in  $\text{Mo}$  and  $\text{W}$  but not in  $\text{Cr}, \text{Ru}$  or  $\text{Re}$ .

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### 1. Introduction

The olefin metathesis reaction has attracted widespread attention in recent years as a versatile carbon–carbon bond-forming method. Metathesis is the metal-catalyzed re-distribution of carbon–carbon double bonds, resulting in the apparent interchanges of carbon atoms between two pairs of bonds. Formally, metathesis involves a simultaneous cleavage of two olefin double bonds, followed by the formation of alternate bonds.

Exchange of the groups around the double bond results in several outcomes: straight swapping of groups between two acyclic olefins (cross-metathesis), closure of large rings (ring-closing metathesis), formation of dienes from cyclic and acyclic olefins (ring-opening metathesis), polymerization of cyclic olefins (ring-opening metathesis polymerization), and polymerization of acyclic dienes (acyclic diene metathesis polymerization) [1]. The power of olefin metathesis is that it transforms the carbon–carbon double bond, a functional group that is unreactive toward many reagents that react with other functional groups.

Olefin metathesis has a variety of applications. Key among them include the use of ring-opening metathesis polymerization to make functionalized polymers, the syntheses of small to large heterocyclic

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systems by ring-closing metathesis, and the cross-metathesis of olefins with pendant functional groups [1] Olefin metathesis opens up new industrial routes to important petrochemicals, oleochemicals, polymers and specialty chemicals [2–5].

The work of Herrison and Chauvin [6] established that metal-alkylidene (carbene) complexes play a pivotal role in transition-metal-catalyzed olefin metathesis, an exchange between a metal carbene and an olefin being a fundamental step of the process. The carbene complex is recognized as the active chain-carrying catalyst that reacts with an olefin to form a metallacyclobutane intermediate that decomposes to form the product olefin. The olefins add, one at a time, to the metal-alkylidene complex *in situ* to form a metallacyclobutane intermediate that breaks apart to form a new olefin and a new metal carbene, which propagates the reaction.

The Herrison–Chauvin mechanism has been established through detailed study of isotopic scrambling [7–10], the synthesis of metallocarbonyl complexes [11–13] and metallacyclobutane [14–18] and by the analysis of the character of polymeric products of cyclo-olefins [19].

The Herrison–Chauvin mechanism of olefin metathesis has also been the subject of a number of theoretical and experimental studies. Eisenstein and co-workers have carried out Extended Hückel [20] and *ab initio* Hartree–Fock [21] studies on the subject. Goddard and Rappé [22] have reported a GVB study of the reaction between  $\text{Cl}_4\text{Mo}=\text{CH}_2$  and ethylene in which the formation of the metallacycle was found to be endothermic. However, when the same reaction was re-calculated it was found to be exothermic [23]. Rappé and Goddard [24] have used the results of *ab initio* GVB and CI theoretical studies to examine the thermochemistry and mechanisms for metathesis of olefins by Cr and Mo complexes and concluded that in activating metal chlorides it is essential to have spectator metal-oxo bonds. Sodupe et al. [25] performed an *ab initio* Hartree–Fock study of the reaction between the  $\text{Cl}_4\text{Mo}=\text{CH}_2$  complex and ethylene and found the formation of the metallacyclobutane to be exothermic. A GVB study found no activation barrier for the interconversion of titanium alkylidene-olefin complex  $\text{Cl}_2\text{TiC}_3\text{H}_6$ , where the metallacyclobutane was found to be 12 kcal/mol more stable than the olefin-alkylidene complex [26,27]. Cundari and Gordon [28] performed an *ab initio* analysis of the electronic structure of high-valent, transition-metal alkylidenes as models for olefin metathesis catalysts and observed that the M–C bond is more polarized in a  $\text{M}^+=\text{C}^-$  fashion for the W methylidene than the Mo–C bond of the Mo methylidene analog is and concluded that the greater polarization correlates with greater metathesis activity exhibited by the W alkylidene metathesis catalysts when compared to Mo analogs.

Grubbs et al. [29,30] and Hoveyda et al. [31] have used ruthenium carbene complexes  $\text{Cl}_2(\text{PR}_3)_2=\text{CHR}'$  to carry out the metathesis of a number of different olefins such as strained and low-strain olefins, oxocyclic olefins and straight-chain alkenes. In systematic studies of the mechanism of olefin metathesis involving the  $\text{Cl}_2(\text{PCy}_3)_2\text{Ru}=\text{CHPh}$  complex, these workers [32,33] found out that the most active species should be a 14-electron monophosphinic complex (with the biphosphinic complex much less active) and that the metallacyclobutane is an intermediate. However, in the work of Chen et al. [34], experimental observations obtained in the gas phase by electrospray ionization tandem mass spectroscopy are consistent with a reaction profile where the metallacyclobutane is a transition state rather than an intermediate. Cavallo [35] has carried out density functional theory study of the ruthenium-catalyzed olefin metathesis reactions and found, *inter alia*, that the metallacyclobutane structures represented minimum energy situations along the reaction coordinate, and are of slightly higher energy with respect to the corresponding olefin-bound

intermediates in the case of the phosphane-based systems, while they are slightly more stable than the olefin adducts in the case of the NHC-based systems. Bernardi et al. [36] carried out a theoretical investigation at the DFT B3LYP level of theory on the mechanism of the metathesis of ethylene catalyzed by Grubbs complexes,  $\text{Cl}_2(\text{PH}_3)_2-\text{Ru}=\text{CH}_2$  and  $\text{Cl}_2(\text{PPh}_3)_2\text{Ru}=\text{CH}_2$ , and found, among other things, that the primary active catalytic species is the metal-carbene complex  $(\text{PR}_3)_2\text{Cl}_2-\text{Ru}=\text{CH}_2$  and not the carbenoid complex  $(\text{PR}_3)_2\text{Cl}-\text{Ru}-\text{CH}_2\text{Cl}$  which was found to be significantly higher in energy (by 18.45 and 19.26 kcal/mol for the two model systems), and that cyclopropanation is disfavored compared to metathesis since the former requires the overcoming of larger activation barriers than those found for the latter. Eisenstein et al. [37] carried out gas phase DFT B3PW91 calculations on the reactivity of ethylene with model systems  $\text{M}(\equiv\text{NR})(=\text{CHCH}_3)$  (X)(Y) [M = Mo, W, Re; R = methyl, phenyl; X =  $\text{CH}_2-\text{CH}_3$ ,  $\text{OCH}_3$ ,  $\text{OSiH}_3$ ; and Y =  $\text{CH}_2\text{CH}_3$ ,  $\text{OCH}_3$ ,  $\text{OSiH}_3$ ] and found out that the factors controlling the detailed shape of the energy profiles are the energy of distortion of the tetrahedral catalyst and the stability of the metallacycle intermediate, which is controlled by the M–C bond strength. They also found that unsymmetrical catalysts (X ≠ Y) were systematically more efficient for all systems (Mo, W, Re) and that overall, the Re complexes were less efficient than the Mo and W catalysts, except when Re is unsymmetrically substituted. Yüksel et al. [38] investigated a catalytic system consisting of tungsten carbene generated from  $\text{WCl}_6$  and atomic carbon for the metathesis of 1-octene at the B3LYP/extended LAN2DZ level of theory and found that the formation of the catalytically active heptylidene is energetically favored in comparison to the formation of methylidene, while the degenerative and productive metathesis steps are competitive. They also found that solvent effects on the metathesis reactions were minor and solvation does not cause any change in the directions of the overall metathesis reactions. Tia and Adei [39] have explored the reactions of  $\text{Cl}_4\text{MCH}_2$  (M = Cr, Mo, W, Ru, Re) with ethylene as models of potential chain-carrying catalysts and olefins respectively in transition metal-catalyzed olefin metathesis reactions at the DFT B3LYP/LAC-VP\* level of theory, aimed at elucidating the metathesis activity of these complexes and delineating the factors responsible for any difference in metathesis activity. They found that in  $\text{Cl}_4\text{MCH}_2$  (M = Cr, Ru) the carbenoid complexes  $\text{Cl}_3\text{MCH}_2-\text{Cl}$ , which did not favor the formation of metallacyclobutanes, were more stable than the carbene complexes  $\text{Cl}_4\text{M}=\text{CH}_2$  which favored the formation of metallacyclobutanes, whereas in  $\text{Cl}_4\text{MCH}_2$  (M = Mo, W, Re) the carbene complexes were more stable than the carbenoid complexes. It was thus concluded that even though the formation of the metallacyclobutane from the carbene complex is a low-barrier process in each of the metals studied, the  $\text{Cl}_4\text{MCH}_2$  (M = Cr, Ru) complexes are precluded from promoting olefin metathesis due to the stability of the inactive carbenoid complexes over the active carbene complexes in the Cr and Ru systems.

Rappé et al. [22] have used the results of a GVB *ab initio* theoretical mechanistic study to suggest that the oxo-alkylidene complex  $\text{Cl}_2(\text{O})\text{M}=\text{CH}_2$  would favor formation of metallacycles because of conversion of the spectator metal-oxo double-bond in the reactant to a metal-oxo triple bond in the product. The work herein reported is an extension of the work reported earlier [39] to involve the oxo-alkylidene complexes  $\text{Cl}_2(\text{O})\text{M}=\text{CH}_2$  (M = Cr, Mo, W, Ru, Re) as potential chain-carrying catalysts that could react with an olefin to form metallacyclobutanes in olefin metathesis, based on the work of Rappé et al. [22]. It explores whether oxo-alkylidene complexes could be used as catalysts in olefin metathesis, by investigating the productive cycle and potential side reactions. Various modes of reaction of ethylene with metal oxo-alkylidenes are considered in the study.

## 2. Details of calculations

All calculations were carried out with the SPARTAN '06 V112 and SPARTAN '08 V120 Molecular Modeling programs [40] at the DFT B3LYP/LACVP\* and MO6/LACVP\* levels of theory. The LACVP\* basis set is a relativistic effective core-potential that describes the atoms H–Ar with the 6-31G\* basis while heavier atoms are modeled with the LANL2DZ basis set which uses the all-electron valence double zeta basis set (D95V), developed by Dunning and Hay [41], for first row elements and the Los Alamos ECP plus double zeta basis set developed by Wadt and Hay for the atoms Na–La, Hf–Bi [42–44].

The starting geometries of the molecular systems were constructed using SPARTAN's graphical model builder and minimized interactively using the sybyl force field [45]. All geometries were fully optimized at both the B3LYP/LACVP\* and MO6/LACVP\* levels of theory without any symmetry constraints. The optimized geometries were subjected to full frequency calculations to verify the nature of the stationary points. Equilibrium geometries were characterized by the absence of imaginary frequencies. The transition state structures were located by a series of constrained geometry optimizations in which the forming- and breaking-bonds were fixed at various lengths while the remaining internal coordinates were optimized. The approximate stationary points located from such a procedure were then fully optimized using the standard transition state optimization procedure in SPARTAN. All first-order saddle-points were shown to have a Hessian matrix with a single negative eigenvalue, characterized by an imaginary vibrational frequency along the reaction coordinate. All the computations were performed on Dell Precision T3400 Workstation computers.

## 3. Results and discussion

The optimized geometries and the relative energies of the main stationary points involved in the reaction between  $\text{Cl}_2(\text{O})\text{CrCH}_2$

and ethylene are shown in Figs. 1 and 2 respectively and Tables 1 and 2. The Cr oxo-methylidene complex **R1-Cr** has Cs symmetry. At the DFT B3LYP/LACVP\* level the Cr=O and Cr=C bond lengths are 1.536 Å and 1.761 Å respectively and the two Cr–Cl bond lengths are 2.150 Å each while at the MO6 level the Cr=O and Cr=C bond lengths are 1.531 Å and 1.744 Å respectively and the two Cr–Cl bond lengths are 2.128 Å each. A carbenoid **R2-Cr** is also located on the reaction surface and is found to be less stable than the carbene minimum by 3.60 kcal/mol at the B3LYP level and 12.74 kcal/mol at the MO6 level.

The formation of the metallacyclobutane **pdt1-Cr** by [2+2] addition of ethylene across the Cr–C bond of **R1-Cr** through transition state **TS1-Cr** has an activation barrier of 12.10 kcal/mol and exothermicity of 14.30 kcal/mol at the B3LYP level and 4.65 kcal/mol and 22.19 kcal/mol respectively at the MO6 level (Fig. 2). The metallacycle is symmetric with respect to the C–C and Cr–C bonds. Rappé et al. [22] had found, by *ab initio* GVB calculations, that the formation of **pdt1-Cr** is exothermic by 20 kcal/mol.

The formation of product **pdt2-Cr** by [2+2] addition of ethylene across the Cr–O bond of **R1-Cr** through transition state **TS2-Cr** has a barrier of 27.42 kcal/mol and endothermicity of 24.01 kcal/mol at the B3LYP level and 30.11 and 13.58 kcal/mol respectively at the MO6 level. Thus the [2+2] addition of ethylene across the Cr–C bond is more favorable, both kinetically and thermodynamically, than addition across the Cr–O bond. The early transition state **TS2-Cr** is a highly asynchronous one. In the work of Rappé et al. this reaction is reported to be 12 kcal/mol endothermic.

The [3+2] addition of ethylene across the Cr–O and Cr–C bonds of **R1-Cr** involves transition state **TS3-Cr**, with a barrier of 9.75 kcal/mol (B3LYP), to form **pdt3-Cr** which is 30.54 kcal/mol exothermic (Fig. 2). The MO6 calculations gave a barrier of 1.12 kcal/mol and an endothermicity of 13.58 kcal/mol. The [3+2] addition across the Cr–O and Cr–Cl bonds has a much higher activation barrier of 27.45 kcal/mol and the resulting product **pdt4-Cr** is 9.99 kcal/mol endothermic by B3LYP calculations.

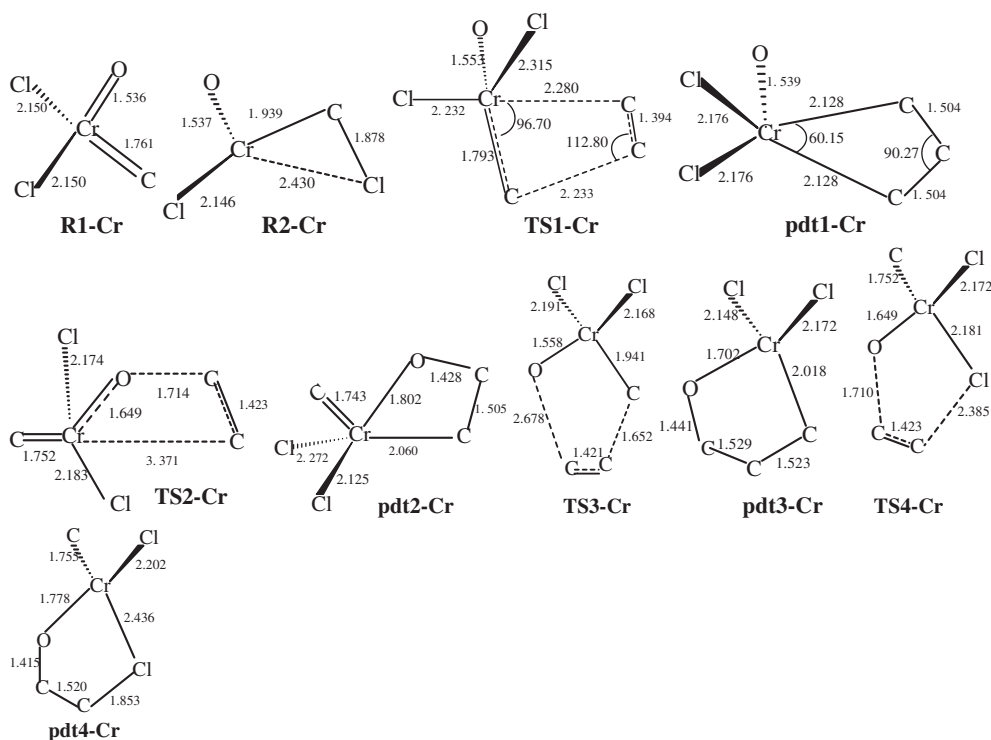


Fig. 1. Optimized geometries (B3LYP) of the main stationary points involved in the reaction of  $\text{Cl}_2(\text{O})\text{CrCH}_2$  with ethylene. Distances in Å and angles in degrees.

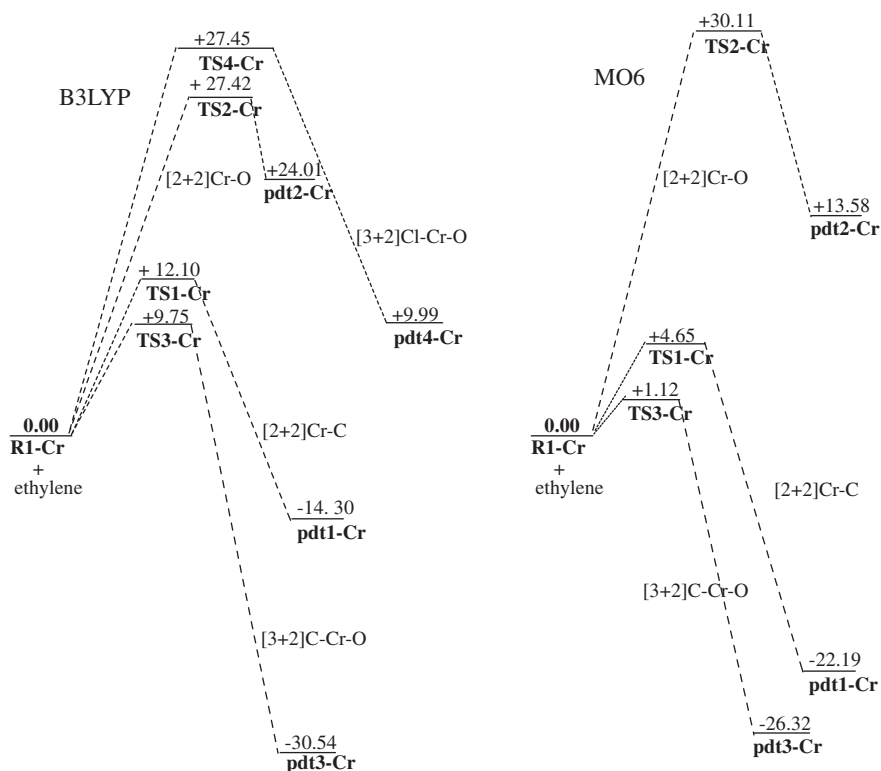


Fig. 2. Energetics of the reactions of  $\text{Cl}_2(\text{O})\text{CrCH}_2$  with ethylene. Relative energies in kcal/mol.

Table 1

Relative energies (in kcal/mol) of the main stationary points for the [2+2] and [3+2] reactions of  $\text{Cl}_2(\text{O})\text{MCH}_2$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}, \text{Ru}, \text{Re}$ ) with ethylene calculated at the B3LYP/LACVP<sup>a</sup> level of theory<sup>a</sup>.

Metal	TS1	TS2	TS3	TS4	pdt1	pdt2	pdt3	pdt4
Cr	+12.10	27.42	+9.75	+27.45	-14.30	+24.01	-30.54	+9.99
Mo	+5.38	+30.67	+26.68	+44.43	-11.38	+18.86	-0.44	+41.69
W	+0.38	+26.25	+39.48	-	-16.49	+19.83	+15.47	-
Ru	+13.78	+17.00	-	+10.17	-31.45	-2.70	-	-16.33
Re	+7.80	+26.66	+11.34	+38.71	-25.70	+7.80	-9.28	+33.44

<sup>a</sup> Energies calculated relative to the respective separated carbene and ethylene reactants.

Table 2

Relative energies (in kcal/mol) of the main stationary points for the [2+2] and [3+2] reactions of  $\text{Cl}_2(\text{O})\text{MCH}_2$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}, \text{Ru}, \text{Re}$ ) with ethylene calculated at the MO6/LACVP<sup>a</sup> level of theory<sup>a</sup>.

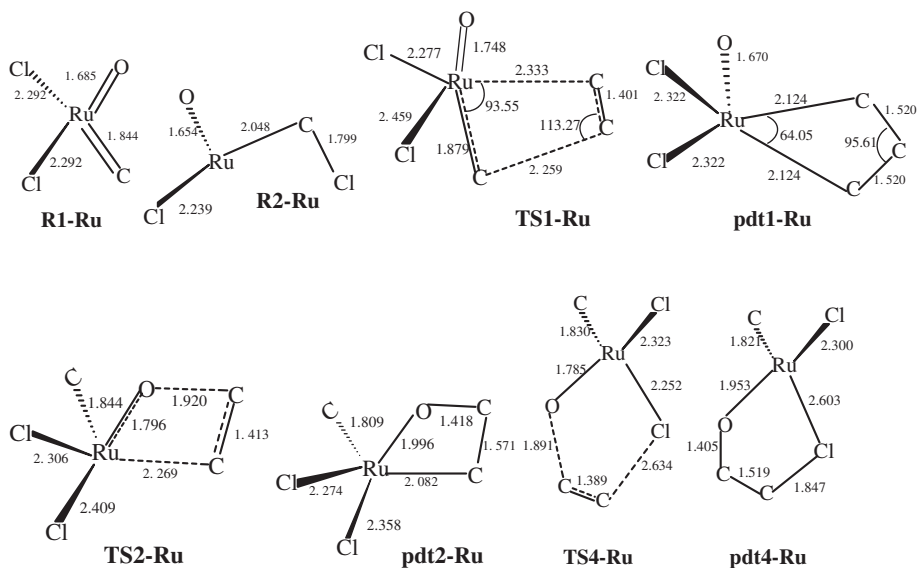
Metal	TS1	TS2	TS3	TS4	pdt1	pdt2	pdt3	pdt4
Cr	+4.65	+30.11	+1.12	-	-22.19	+13.58	-26.32	+17.60
Mo	+2.69	+23.64	+16.58	+41.78	-19.86	+9.16	-7.09	+35.65
W	+0.28	+19.09	+30.79	-	-25.92	+11.01	+7.61	-
Ru	+4.74	+8.57	-	+8.29	-42.57	-16.04	-	-23.23
Re	+0.58	+19.92	+4.64	+35.55	-35.39	-1.18	-17.60	+25.39

<sup>a</sup> Energies calculated relative to the respective separated carbene and ethylene reactants.

Thus the most favorable pathway, kinetically and thermodynamically, is the [3+2] addition of ethylene across the Cr–O and Cr–C bonds of **R1-Cr**. Since the [3+2] addition is more favorable than the first step of the olefin metathesis reaction, i.e. the formation of the metallacyclobutane through [2+2] addition across the Cr–C bond of **R1-Cr** (Fig. 2), the complex  $\text{Cl}_2(\text{O})\text{CrCH}_2$  may not promote olefin metathesis. However, since the lowest-barrier side reaction is only 2.35 kcal/mol (B3LYP) and 3.43 kcal/mol (MO6) more favorable than the metathesis pathway, metathesis may occur to some extent. This is in contrast to the  $\text{Cl}_4\text{CrCH}_2$  system [39] where the metathesis pathway is clearly disfavored.

In the earlier study [39] it was concluded that the  $\text{Cl}_4\text{CrCH}_2$  complex may not promote metathesis because the carbenoid complex  $\text{Cl}_3\text{CrCH}_2\text{-Cl}$  which was found not to favor the formation of metallacyclobutanes was computed to be more stable than the carbene complexes  $\text{Cl}_4\text{Cr=CH}_2$ , the active species of the process, a situation that will lead to the reaction surface being populated by the inactive species rather than the active species of the process.

DFT optimization of the Ru oxo-alkylidene intermediate gave structure **R1-Ru**, which has a Ru–C bond length of 1.844 Å, Ru–O bond length of 1.685 Å and the two Ru–Cl bond lengths at 2.292 Å each at the B3LYP level (Fig. 3).



**Fig. 3.** Optimized geometries (B3LYP) of the main stationary points involved in the reaction of  $\text{Cl}_2(\text{O})\text{RuCH}_2$  with ethylene. Distances in Å and angles in degrees.

A carbenoid minimum **R2-Ru** has been located and is 4.07 kcal/mol less stable than the carbene. The activation barrier for the formation of metallacyclobutane **pdt1-Ru** by [2+2] addition of the olefinic bond across the Ru—C bond of **R1-Ru** through transition state **TS1-Ru** has an activation barrier of 13.78 kcal/mol and an exothermicity of 31.45 kcal/mol by B3LYP calculations and a barrier of 4.74 kcal/mol and exothermicity of 42.57 kcal/mol by MO6 calculations (Fig. 4).

The barrier for [2+2] addition across the Ru—O bond of **R1-Ru** through transition state **TS2-Ru** is 17.00 kcal/mol by B3LYP calculations and 8.57 kcal/mol by MO6 calculations, leading to product **pdt2-Ru** which is 2.70 kcal/mol and 16.04 kcal/mol exothermic by B3LYP and MO6 calculations respectively. Thus, of the [2+2] addition pathways, addition across the Ru—C bond is more favorable, both kinetically and thermodynamically, than addition across the Ru—O bond.

Along the [3+2] pathway, addition of ethylene across the Ru—O and Ru—Cl bonds of **R1-Ru** through **TS4-Ru** has a barrier of 10.17 kcal/mol with the resulting product **pdt4-Ru** being 16.33 kcal/mol exothermic at the B3LYP level. At the MO6 level the barrier is 8.29 kcal/mol and the exothermicity is 23.23 kcal/mol. Attempts at locating a transition state or product corresponding to the [3+2] addition across the Ru—O and Ru—C bonds on the surface were not successful.

The B3LYP results indicate that the [3+2] addition pathway will most likely interfere with the metallacyclobutane formation because it is slightly more favorable kinetically than the [2+2] addition across the Ru—C bond of **R1-Ru**. However, since the barrier difference is not very much (3.61 and 3.55 kcal/mol respectively at the B3LYP and MO6 levels), metallacyclobutane formation may still occur. Useful metathesis catalysts should not only have a low barrier for formation of the metallacyclobutane intermediate, but also for its subsequent decomposition through cycloreversion. Since the metallacyclobutane is predicted to be very stable, its decomposition may not be feasible. Thus the metallacyclobutane intermediate may actually be the final product, i.e. a dead end in the catalytic cycle.

On the Mo reaction surface, the reactant oxo-alkylidene **R1-Mo** (Fig. 5) has a Mo=O bond length of 1.681 Å, Mo=C bond length of 1.883 Å and the two Mo—Cl bond lengths at 2.303 Å each at the B3LYP level of theory. No carbenoid minimum could be located on the surface. The transition barrier for [2+2] addition of ethylene

across the Mo—C bond of **R1-Mo** through transition state **TS1-Mo** is 5.38 kcal/mol, leading to the metallacycle **pdt1-Mo** which is 11.38 kcal/mol exothermic, by B3LYP calculations. By MO6 the barrier is 2.69 kcal/mol and the exothermicity is 19.86 kcal/mol (Fig. 6). Rappé et al. [22] found this reaction to be 24 kcal/mol exothermic. Compared with the corresponding Cr-system this reaction is more favorable kinetically, but slightly less so thermodynamically. The [2+2] addition of ethylene across the Mo—O bond of **R1-Mo** has a barrier of 30.67 kcal/mol at the B3LYP level, which is about six times higher than the barrier for addition across the Mo—C bond and 23.64 kcal/mol by MO6 calculations. The resulting metallacycle **pdt2-Mo** is 18.86 kcal/mol and 9.16 kcal/mol endothermic at the B3LYP and MO6 levels respectively. Thus addition across the Mo—C bond is more favorable, both kinetically and thermodynamically, than addition across the Mo—O bond.

The [3+2] addition across the Mo—C and Mo—O bonds through transition state **TS3-Mo** has a barrier of 26.68 kcal/mol at the B3LYP level and 16.58 kcal/mol at the MO6 level, leading to a five-membered product **pdt3-Mo** which is 0.44 kcal/mol exothermic at the B3LYP level and 7.09 kcal/mol exothermic at the MO6 level while the [3+2] addition across the Mo—O and Mo—Cl bonds of **R1-Mo** through transition state **TS4-Mo** has a much higher barrier of 44.43 kcal/mol at the B3LYP level and 41.78 kcal/mol at the MO6 level, leading to product **pdt4-Mo** which is very endothermic (+41.69 kcal/mol by B3LYP and +35.65 kcal/mol by MO6). Therefore, in the Mo complex the [2+2] addition of ethylene across the Mo—C bond of **R1-Mo**, which is the first step of the olefin metathesis reaction, is the most favorable reaction pathway. With a barrier difference of 19.30 kcal/mol (B3LYP) and 13.82 kcal/mol (MO6) between the metallacyclobutane formation pathway and the lowest-barrier side reaction, the preference of the metathesis pathway over the potential side reactions is clearly unambiguous. The selectivity of the olefin metathesis reaction over the side reactions is higher in the  $\text{Cl}_2(\text{O})\text{MoCH}_2$  complex than in the  $\text{Cl}_4\text{MoCH}_2$  complex [39] where the difference in activation barriers between the metathesis pathway and the lowest-barrier side reaction is only 1.58 kcal/mol at the B3LYP level. Thus the presence of the oxo group enhances the selectivity of the metathesis reaction in the Mo complexes.

The W oxo-alkylidene reactant **R1-W** (Fig. 7) has a W=O bond length of 1.688 Å, a W=C bond length of 1.886 Å and the two W—Cl bond lengths at 2.299 Å each at the B3LYP level of theory.



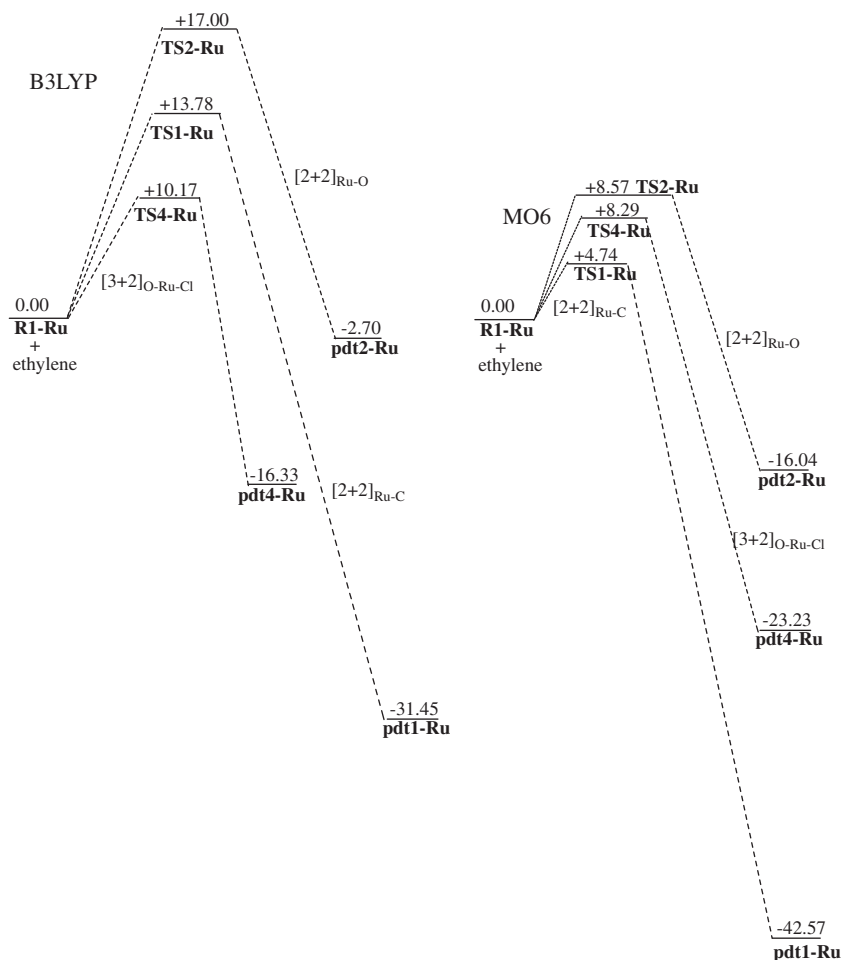


Fig. 4. Energetics of the reactions of  $\text{Cl}_2(\text{O})\text{RuCH}_2$  with ethylene. Relative energies in kcal/mol.

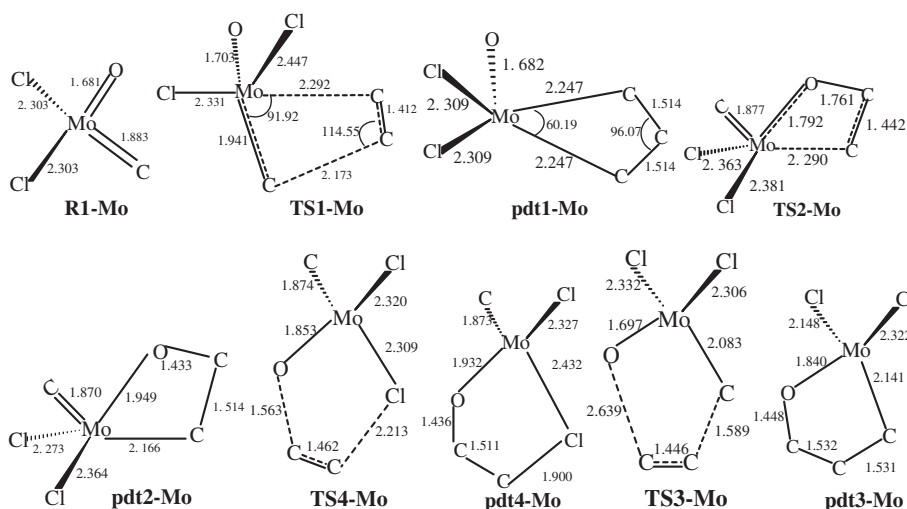


Fig. 5. Optimized geometries (B3LYP) of the main stationary points involved in the reaction of  $\text{Cl}_2(\text{O})\text{MoCH}_2$  with ethylene. Distances in Å and angles in degrees.

The [2+2] addition of the olefinic bond across the W–C bond of **R1-W** through transition state **TS1-W** with activation barrier of 0.38 kcal/mol at the B3LYP level and 0.28 kcal/mol at the MO6 level, leads to the formation of metallacyclobutane **pdt1-W**, which is 16.49 kcal/mol and 25.92 kcal/mol exothermic respectively at the B3LYP and MO6 levels (Fig. 8). In the work of Rappé et al. [22] this reaction is found to be 18 kcal/mol exothermic.

The activation energy for [2+2] addition across the W–O bond of **R1-W** through transition state **TS2-W** is 26.25 kcal/mol at the B3LYP level and 19.09 kcal/mol at the MO6 level, resulting in a metallacycle **pdt2-W** which is 19.83 kcal/mol and 11.01 kcal/mol endothermic respectively at the B3LYP and MO6 levels. Thus addition across the W–C is far more favored, both kinetically and thermodynamically, than addition across the W–O bond.

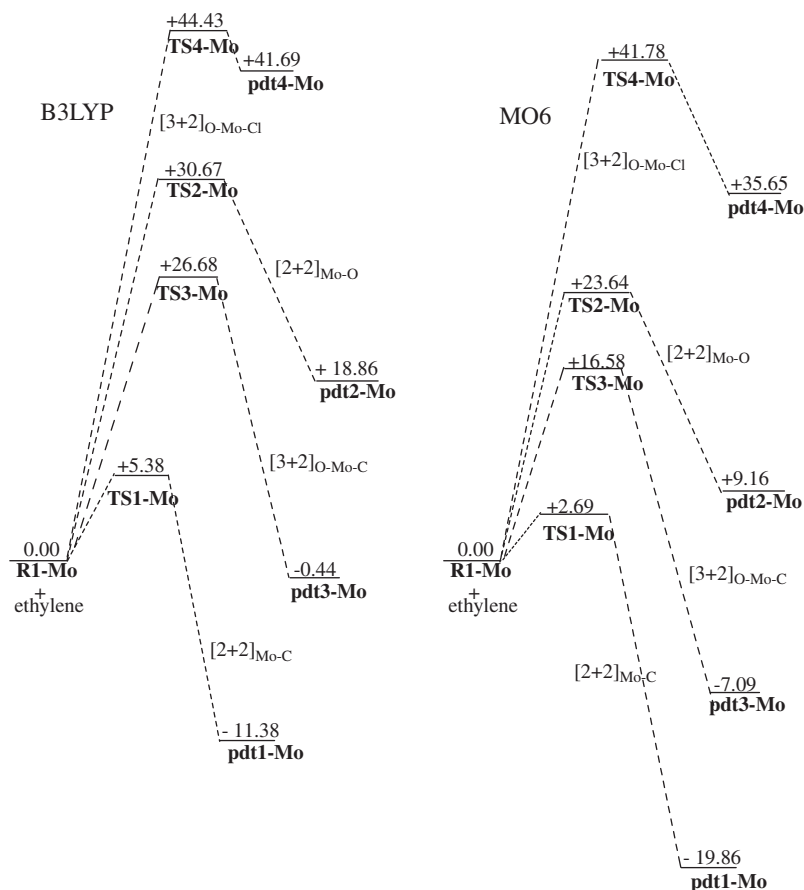


Fig. 6. Energetics of the reactions of  $\text{Cl}_2(\text{O})\text{MoCH}_2$  with ethylene. Relative energies in kcal/mol.

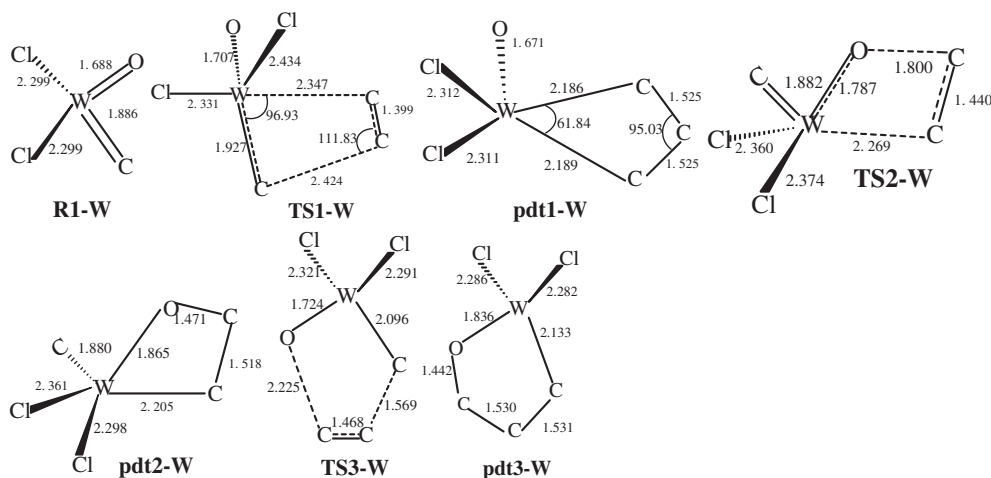


Fig. 7. Optimized geometries (B3LYP) of the main stationary points involved in the reaction of  $\text{Cl}_2(\text{O})\text{WCH}_2$  with ethylene. Distances in Å and angles in degrees.

Along the [3+2] pathway, addition across the W–O and W–C bonds of **R1-W** through transition state **TS3-W** has a barrier of 39.48 kcal/mol at the B3LYP level and 30.79 kcal/mol at the MO6 level, leading to a five-membered ring product **pdt3-W** which is 15.47 kcal/mol and 7.61 kcal/mol endothermic at the B3LYP and MO6 levels respectively. No product or transition state could be located for the [3+2] addition across the W–O and W–Cl bonds.

Of the three possible addition pathways, the [2+2] addition of ethylene across the W–C bond, which is the first step of the olefin metathesis reaction, is the most favorable one. The metathesis

pathway has an activation barrier of 25.87 kcal/mol (B3LYP) and 18.81 kcal/mol (MO6) lower than the lowest-barrier side reactions: the possible side reactions are not competitive with the olefin metathesis reaction, just as has been observed for the Mo system. This indicates that the W complex will be able to promote olefin metathesis.

The optimized geometries and relative energies of the main stationary points involved in the reaction of the Re oxo-methylidene complex  $\text{Cl}_2(\text{O})\text{ReCH}_2$  with ethylene are shown in Figs. 9 and 10 respectively. The Re complex displays a doublet ground state elec-

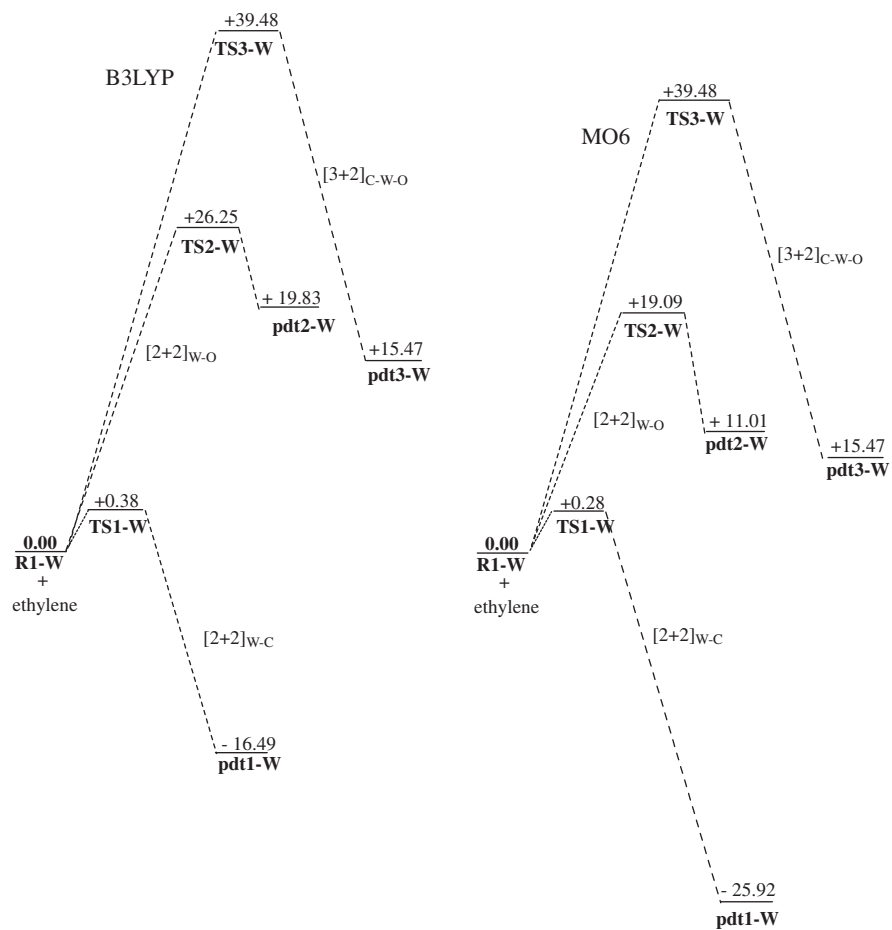


Fig. 8. Energetics of the reactions of  $\text{Cl}_2(\text{O})\text{WCH}_2$  with ethylene. Relative energies in kcal/mol.

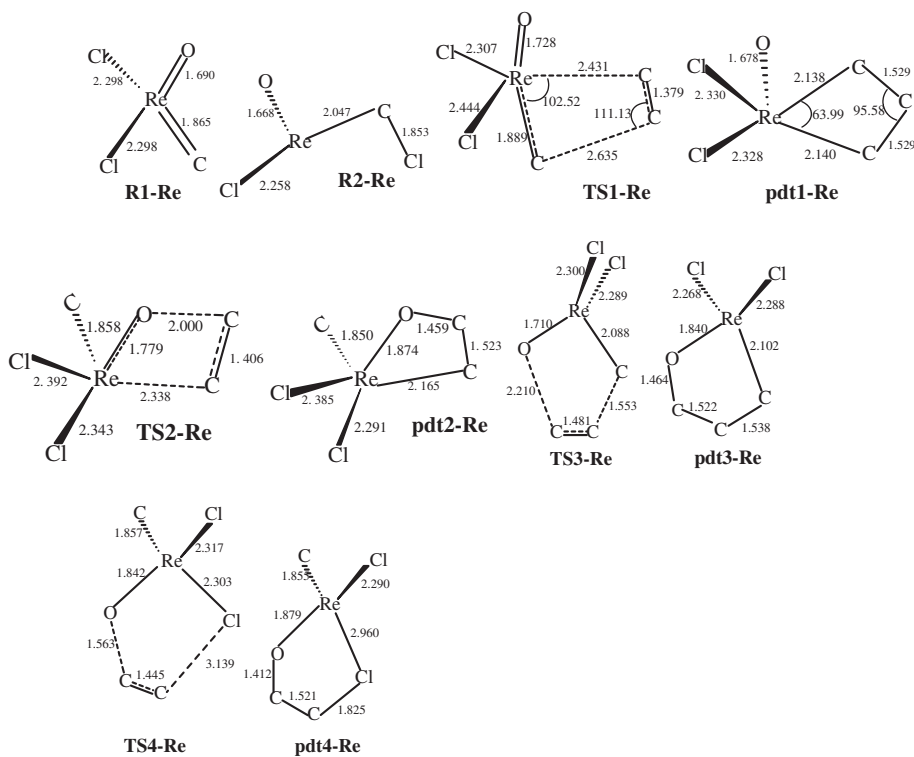


Fig. 9. Optimized geometries of the main stationary points involved in the reaction of  $\text{Cl}_2(\text{O})\text{ReCH}_2$  with ethylene. Distances in Å and angles in degrees.



tronic structure rather than a singlet structure. It also displays a quartet structure but this is of higher energy than the doublet structure. The doublet oxo-methylidene reactant **R1-Re** has the two Re–Cl bonds at 2.298 Å, the Re–O bond at 1.690 Å and the Re–C bond at 1.865 Å at the B3LYP level. The quartet reactant which displays slightly longer bonds than the doublet structure is 77.33 kcal/mol and 35.67 kcal/mol less stable than the doublet structure at the B3LYP and MO6 levels respectively. Since the structures on the doublet PES were found to be more stable than those obtained on the quartet PES and some of the key structures such as the metallacyclobutane could not be located on the quartet PES, only the doublet PES was explored further. An oxo-carbenoid **R2-Re** that has been optimized is found to be 29.33 kcal/mol and 27.53 kcal/mol less stable than the carbene reactant at the B3LYP and MO6 levels respectively.

The formation of the metallacyclobutane **pdt1-Re** by [2+2] addition of ethylene across the Re–C bond of  $\text{Cl}_2(\text{O})\text{ReCH}_2$  through transition state **TS1-Re** has an activation barrier of 7.80 kcal/mol and an exothermicity of 25.70 kcal/mol at the B3LYP level, and 0.58 kcal/mol and 35.39 kcal/mol at the MO6 level respectively. Thus at the B3LYP level this barrier is lower than the corresponding barriers for the Cr (12.10 kcal/mol) and Ru (13.78 kcal/mol) complexes, comparable with the barrier in the Mo system (5.38 kcal/mol) but higher than the barrier in the W system (0.38 kcal/mol) while at the MO6 level it is lower than Cr (4.65 kcal/mol), Mo

(2.69 kcal/mol) and Ru (4.74 kcal/mol), and comparable with W (0.28 kcal/mol). The exothermicity is also higher than the corresponding exothermicities for all the complexes except for Ru at both levels of theory. The Re–O bond length in the reactant, like all the other reactant M–O bonds, does not undergo any change in the formation of the metallacyclobutane product.

At the B3LYP level, the formation of product **pdt2-Re** by [2+2] addition of ethylene across the Re–O bond of  $\text{Cl}_2(\text{O})\text{Re}=\text{CH}_2$  through transition state **TS2-Re** is 7.80 kcal/mol endothermic and has an activation barrier of 26.66 kcal/mol. This barrier is comparable with the barriers of 27.42, 30.67, and 26.25 kcal/mol found for the corresponding reactions in the Cr, Mo, and W complexes respectively but higher than the barrier of 17.00 kcal/mol found for the Ru complex. The product **pdt2-Re** is also more stable than the corresponding products in the Cr, Mo, and W complexes but 10.50 kcal/mol less stable than the Ru product. At the MO6 level, this reaction is slightly exothermic (–1.18 kcal/mol) and has an activation barrier of 19.92 kcal/mol, a barrier which is comparable with the barriers for the corresponding reaction in W (19.09 kcal/mol) and Mo (23.64 kcal/mol), lower than the barrier in Cr (3.11 kcal/mol) and higher than the barrier in Ru (8.57 kcal/mol).

The activation barrier for [3+2] addition of ethylene across the Re–C and Re–O bonds of  $\text{Cl}_2(\text{O})\text{ReCH}_2$  through transition state **TS3-Re** is 11.34 kcal/mol at the B3LYP level and 4.64 kcal/mol at the MO6 level. In transition state **TS3-Re** the newly-forming C–C

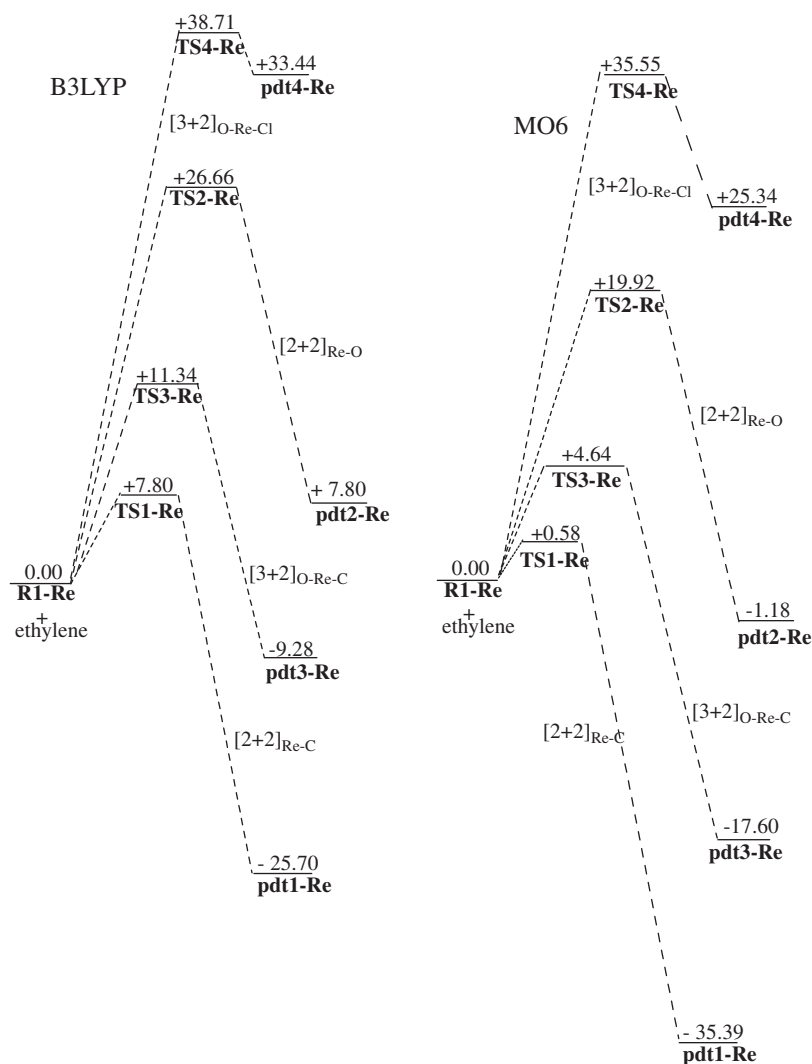
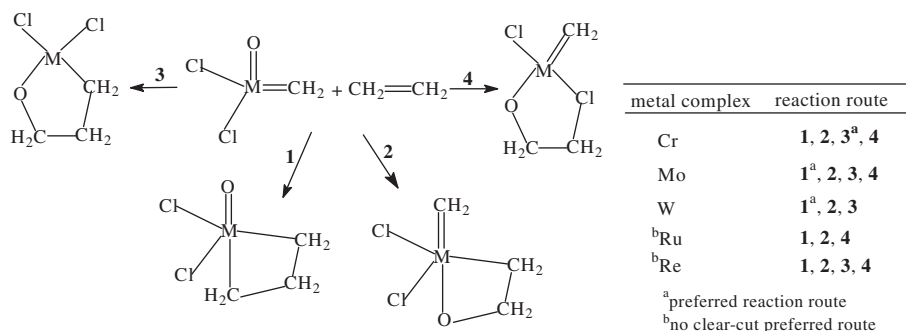


Fig. 10. Energetics of the reactions of  $\text{Cl}_2(\text{O})\text{ReCH}_2$  with ethylene. Relative energies in kcal/mol.



**Fig. 11.** Summary of the preferred reaction routes of  $\text{Cl}_2(\text{O})\text{MCH}_2$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}, \text{Ru}, \text{Re}$ ) with ethylene.

bond is almost formed and thus the critical activity is the forming of the C—O bond. The resulting product **pdt3-Re** is 9.28 kcal/mol and 17.60 kcal/mol exothermic at the B3LYP and MO6 levels respectively. The [3+2] addition across the Re—O and Re—Cl bonds has a much higher barrier (38.71 kcal/mol and 35.55 kcal/mol at the B3LYP and MO6 levels respectively) through transition state **TS4-Re** and the resulting product **pdt4-Re** is very unstable (33.44 kcal/mol and 25.39 kcal/mol endothermic at the B3LYP and MO6 levels respectively). Since the formation of the metallacyclobutane **pdt1-Re** has a lower barrier than all the potential side-reactions, olefin metathesis may be the most favorable pathway in the Re complex. However the metallacyclobutane formation step is only marginally favored (activation barriers lower by just 3.54 kcal/mol (B3LYP) and 4.06 kcal/mol (MO6) than the lowest-barrier side reactions) and therefore the metathesis reaction may not be very selective. Moreover, since the metallacyclobutane is very stable (35.39 kcal/mol by MO6), its decomposition to form the final product may not be feasible and thus metathesis may not occur.

Fig. 11 is a summary of the possible paths for the reactions of the  $\text{Cl}_2(\text{O})\text{MCH}_2$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}, \text{Ru}, \text{Re}$ ) complexes with ethylene. For the reactions of  $\text{Cl}_2(\text{O})\text{MCH}_2$  ( $\text{M} = \text{Mo}, \text{W}, \text{Re}$ ), the pathway leading to the formation of the metallacyclobutane is the most favorable course of reaction whereas in  $\text{Cl}_2(\text{O})\text{CrCH}_2$  this pathway is less favorable compared to the side reactions. In  $\text{Cl}_2(\text{O})\text{RuCH}_2$  the metathesis pathway and the side reactions are competitive. Thus the metathesis reaction will occur preferentially in the Mo and W complexes, and only marginally in the Re complex.

Using the barrier of formation of the metallacyclobutane and the preference of the metallacyclobutane formation over the side-reactions as the criteria for determining metathesis activity, the W complex appears to be the best complex for olefin metathesis reactions, followed by the Mo complex.

The M—O bond lengths in the reactants and the products of [2+2] addition of ethylene to the M—C bonds of  $\text{Cl}_2(\text{O})\text{MCH}_2$  are not significantly different. This is contrary to the conclusions of Rappé and Goddard that the spectator oxo-group double-bond in the reactant is converted to a triple bond in the product [22], since such a conversion will lead to a decrease in the Cr—O bond length.

#### 4. Conclusion

The activation barriers for the formation of the metallacyclobutane, a key intermediate in the olefin metathesis reaction according to the Herrison–Chauvin mechanism, were found to decrease in the order: Ru (13.78 kcal/mol) > Cr (12.10 kcal/mol) > Re (7.80 kcal/mol) > Mo (5.80 kcal/mol) > W (0.38 kcal/mol). In  $\text{Cl}_2(\text{O})\text{MCH}_2$  ( $\text{M} = \text{Cr}, \text{Ru}$ ), the potential chain-terminating side reactions are more favorable than the olefin metathesis reaction whereas in  $\text{Cl}_2(\text{O})\text{MCH}_2$  ( $\text{M} = \text{Mo}, \text{W}, \text{Re}$ ) the olefin metathesis route is the most favorable pathway. The difference between the metallacyclobu-

tane formation pathway and the lowest-barrier side reactions in the W, Mo, and Re complexes decrease in the order: W (25.87 kcal/mol) > Mo (19.30 kcal/mol) > Re (3.54 kcal/mol), clearly establishing that in the W and Mo complexes the metathesis pathway is highly favored over the side reactions whereas in the Re complex the preference is only marginal. Thus metathesis may occur when  $\text{M} = \text{Mo}$  and  $\text{W}$ , whereas  $\text{Cl}_2(\text{O})\text{CrCH}_2$ ,  $\text{Cl}_2(\text{O})\text{RuCH}_2$  and  $\text{Cl}_2(\text{O})\text{ReCH}_2$  Re are borderline cases. Moreover, in the Re and Ru complexes, the metallacyclobutane, if formed at all, is predicted to be very stable and may not easily undergo cycloreversion, to form the final products.

Comparison of the results of this study (i.e. the B3LYP energetics since Ref. [39] employed only the B3LYP level) with those reported by Tia and Adei [39] indicate that replacing  $\text{Cl}_4\text{MCH}_2$  with  $\text{Cl}_2(\text{O})\text{MCH}_2$  as models of the carbene complex raises the activation barriers for the metallacyclobutane formation reaction in the Cr, Ru and Re complexes, but lowers it in the W complex. There is no significant change in activation barriers in the Mo complex; however the selectivity of the metathesis reaction is higher with the  $\text{Cl}_2(\text{O})\text{MoCH}_2$  complex than with the  $\text{Cl}_4\text{MoCH}_2$ . Thus the presence of the double bond oxo group in the carbene complexes will most likely increase metathesis activity in the Mo and W complexes but not in the Re complex. Also the metathesis reaction is less disfavored in the  $\text{Cl}_2(\text{O})\text{CrCH}_2$  complex than it is in the  $\text{Cl}_4\text{CrCH}_2$  complex. The trend in metathesis activity between the Mo, W and Re complexes in this study is consistent with the trend found in the work of Eisenstein et al. [37] on the  $\text{M}(\equiv\text{NR})(=\text{CHCH}_3)(\text{X})(\text{Y})$  ( $\text{M} = \text{Mo}, \text{W}, \text{Re}$ ;  $\text{R} = \text{methyl}, \text{phenyl}$ ;  $\text{X} = \text{CH}_2\text{—CH}_3, \text{OCH}_3, \text{OSiH}_3$ ; and  $\text{Y} = \text{CH}_2\text{CH}_3, \text{OCH}_3, \text{OSiH}_3$ ) system carried out at the DFT B3PW91 level. The W carbene complexes  $\text{Cl}_2(\text{O})\text{WCH}_2$  have been found to be the best complexes for olefin metathesis reactions.

In all the complexes studied, the MO6 calculations gave lower activation barriers and more stable products than the B3LYP calculations for corresponding reactions, the barrier-lowering effect being more pronounced in the metallacyclobutane formation step in each of the complexes. Generally, the two methods gave the same trends in the relative energies of the reactants, transition states and products in each complex, except in Ru where the MO6 method predicts the metallacyclobutane formation step to be more feasible than the [3+2] addition route and the B3LYP method reverses the order by almost the same magnitude.

#### Acknowledgements

The authors are very grateful to the National Council for Tertiary Education (NCTE), Ghana, for financial assistance under the Teaching and Learning Innovation Fund (TALIF-KNUSTR/3/008/2005) to establish a Computational Quantum Chemistry Laboratory at the Department of Chemistry, KNUST, Kumasi, Ghana, where the work was carried out.

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.comptc.2011.05.032.

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