

Density functional theory studies of the mechanistic aspects of olefin metathesis reactions†

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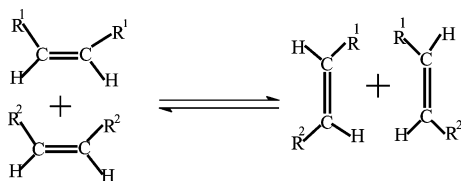
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The potential energy surfaces of the reactions of Cl_4MCH_2 ($\text{M} = \text{Cr}, \text{Mo}, \text{W}, \text{Ru}, \text{Re}$) with ethylene, models of potential chain-carrying catalysts and olefins respectively in the transition metal-catalyzed olefin metathesis reaction, have been explored using density functional theory at the B3LYP/LACVP* level of theory. In Cl_4MCH_2 ($\text{M} = \text{Cr}, \text{Ru}$), the carbenoid complexes $\text{Cl}_3\text{MCH}_2\text{-Cl}$ have been found to be more stable than the corresponding carbene $\text{Cl}_4\text{M=CH}_2$ complexes whereas in Cl_4MCH_2 ($\text{M} = \text{Mo}, \text{W}, \text{Re}$) the carbene complexes are more stable than the carbenoid complexes. The carbenoid complexes have been found not to favor the formation of metallacyclobutanes, a key step in the olefin metathesis reaction according to the Herrison–Chauvin mechanism, indicating that the active species for the metathesis reaction is a carbene complex and not a carbenoid complex. Therefore, even though the formation of metallacyclobutanes through formal [2+2] cycloaddition has been found to be a low-barrier process with each of the metal carbene complexes investigated, metathesis is likely to occur only in Cl_4MCH_2 ($\text{M} = \text{Mo}, \text{W}, \text{Re}$) but not in Cl_4MCH_2 ($\text{M} = \text{Cr}, \text{Ru}$) since the reaction surface in the latter complexes is likely to be populated by the carbenoid complex rather than the carbene complex. In $\text{Cl}_4\text{W=CH}_2$ the kinetic and thermodynamic preference of the productive [2+2] pathway leading to the metallacyclobutane over the [3+2] pathway is unambiguous whereas in Cl_4MoCH_2 the [3+2] pathway is likely to be competitive with the [2+2] pathway. The metallacyclobutane formation in W and Re has been found to have lower barriers than in Mo, suggesting that the W and Re complexes may have a greater metathesis activity than the Mo complex.

Introduction

Metathesis is the metal-catalyzed re-distribution of carbon–carbon double bonds. The reaction describes 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.



Olefin metathesis has become a widely used reaction in organic and polymer chemistry^{1–3} for a number of reasons. First, some olefins are easy to prepare and others require more effort to access. Olefin metathesis allows facile access from the easily prepared olefins to those that are cumbersome to prepare. Second, olefin metathesis reactions either do not generate a by-product or only produce one, such as ethylene, which can be removed by evaporation. Third, olefins are routinely used to interconvert molecules. Olefins are useful largely because they represent the best of two worlds: stability and reactivity. Olefins are stable—they are

typically stored indefinitely without decomposition, and yet they contain a π -bond that is sufficiently reactive to be used in a wide range of transformations.

Olefin metathesis has a variety of applications, including ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM), acyclic diene metathesis polymerization (ADMET), ring-opening metathesis (ROM) and cross-metathesis (CM).⁴ Some of the most impressive achievements include the use of ROMP to make functionalized polymers, the syntheses of small to large heterocyclic systems by RCM, and the CM of olefins with pendant functional groups. Olefin metathesis opens up new industrial routes to important petrochemicals, oleochemicals, polymers and speciality chemicals.⁵

Since the work of Herrison and Chauvin,⁶ it has been generally accepted that metal–alkylidene (carbene) complexes play a pivotal role in transition-metal-catalyzed olefin metathesis. 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 alkenes add, one at a time, to the metal–alkylidene complex *in situ* to form a metallacyclobutane intermediate, which subsequently leads to alkylidene–alkene exchange in the propagation stage (Scheme 1).

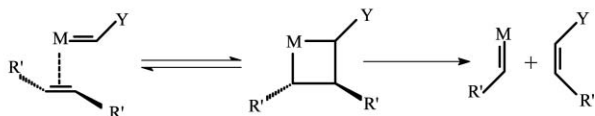
The Herrison–Chauvin mechanism has been established through detailed study of isotopic scrambling,^{7–10} the synthesis of metalloalkylidenes^{11–13} and metallacyclobutanes^{14–18} and by the analysis of the character of polymeric products of cyclo-olefins.¹⁹

The Herrison–Chauvin mechanism of olefin metathesis has also been the subject of a number of theoretical studies. Eisenstein and co-workers have carried out Extended Hückel²⁰ and *ab initio*

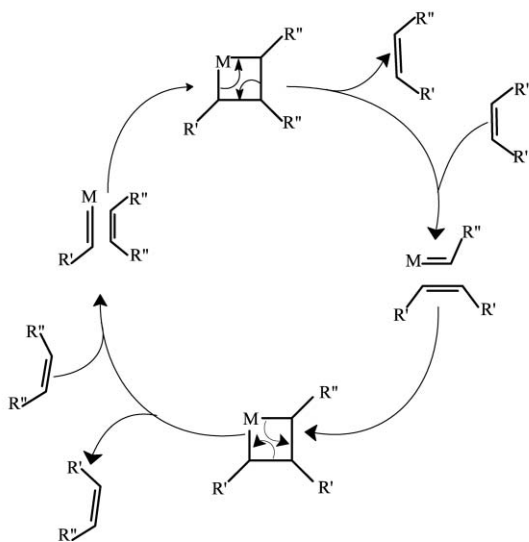
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† Electronic supplementary information (ESI) available: Optimized geometries, absolute energies and symmetry point groups for all the structures reported in the paper. See DOI: 10.1039/c002245d

Initiation:



Catalytic Cycle:



Scheme 1

Hartree–Fock²¹ studies on the subject. Goddard *et al.*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 *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 double-bond spectator oxo group in the reactant to a triple bond in the product. Rappé and Goddard²⁴ have again 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⁻¹ more stable than the olefin–alkylidene complex.^{26,27} Cundari and Gordon²⁸ 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 for the Mo methylidene analogue and concluded that the greater polarization correlates with greater metathesis activity exhibited by the W alkylidene metathesis catalysts when compared to Mo analogues.

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 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. Cavallo³⁵ 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 have 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 $(\text{PR}_3)_2\text{Cl}_2\text{-Ru}=\text{CH}_2$ and not the carbenoid complex $(\text{PR}_3)_2\text{Cl-Ru-CH}_2\text{Cl}$ which was found to be significantly higher in energy (by 18.45 and 19.26 kcal mol⁻¹ 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 $\text{M}(\equiv\text{NR})(=\text{CHCH}_3)(\text{X})(\text{Y})$ [$\text{M} = \text{Mo}, \text{W}$; $\text{R} = \text{methyl, phenyl}$; $\text{X} = \text{CH}_2\text{-CH}_3, \text{OCH}_3, \text{OSiH}_3$; and $\text{Y} = \text{CH}_2\text{CH}_3, \text{OCH}_3, \text{OSiH}_3$] 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 ($\text{X} \neq \text{Y}$) 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 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. To date, no olefin metathesis involving hexavalent chromium complexes has been reported, but the reason for this has not been elucidated.

In this work, the mechanisms of the reactions of the complexes Cl_4MCH_2 ($\text{M} = \text{Cr}, \text{Mo}, \text{W}, \text{Ru}, \text{Re}$) with ethylene are studied theoretically at the DFT B3LYP/LACVP* level of theory with the aim of elucidating the metathesis activity of these complexes and delineating the factors responsible for any difference in metathesis activity. This has been done by exploring the most favorable reaction routes of these complexes with ethylene *vis-à-vis* the [3+2] and [2+2] addition pathways in an attempt to provide insight into

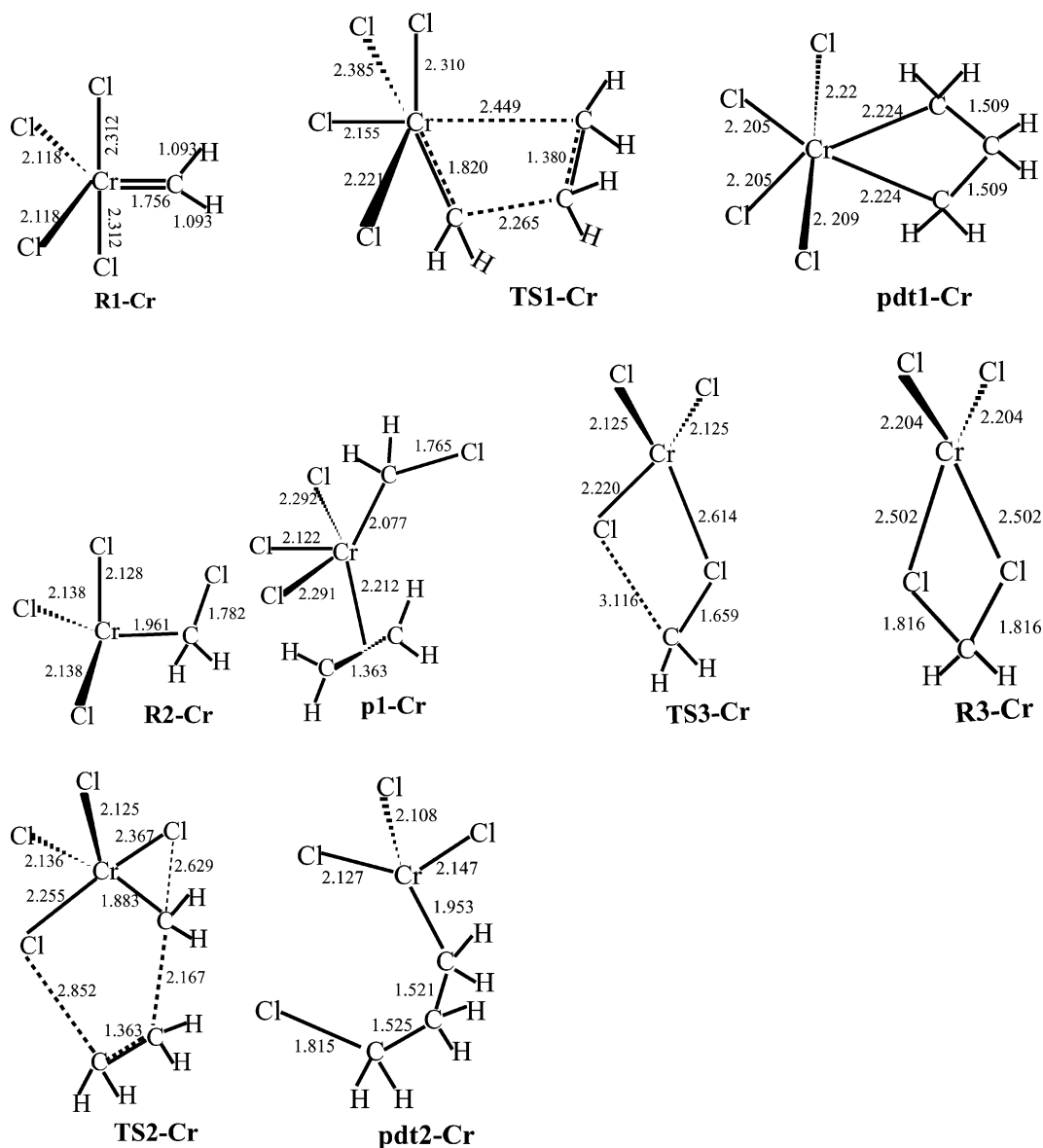


Fig. 1 Optimized geometries of the main stationary points involved in the reaction of Cl_4CrCH_2 with ethylene. Distances in Å and angles in degrees.

this class of reactions, particularly the reasons for the absence of olefin metathesis in hexavalent chromium complexes and the trends in the reactivity of the metal complexes.

Calculation details

All calculations were carried out with the SPARTAN '06 V112 Molecular Modeling program³⁹ at the DFT B3LYP/LACVP* level 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,⁴⁰ 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.^{41–43}

The starting geometries of the molecular systems were constructed using SPARTAN's graphical model builder and minimized interactively using the sybyl force field.⁴⁴ All geometries were fully optimized 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.

Results and discussion

The optimized geometries and relative energies of the main stationary points involved in the reaction between Cl_4CrCH_2 and ethylene are shown in Fig. 1 and Fig. 2, respectively. The DFT geometry optimization of Cl_4CrCH_2 on the singlet potential energy surface (PES) yielded three minima: a trigonal bipyramid carbene structure $\text{Cl}_4\text{Cr}=\text{CH}_2$ (**R1-Cr**) of C_{2v} symmetry in which the methylene ligand occupies an equatorial position on the metal center with the hydrogen atoms in the trigonal planes, a carbenoid complex $\text{Cl}_3\text{CrCH}_2\text{-Cl}$ (**R2-Cr**), which was obtained in an attempt at optimizing the axial methylidene intermediate, and a bridged compound **R3-Cr**. The axial Cr–Cl bonds of **R1-Cr** were found to be 0.194 Å longer than the equatorial Cr–Cl bonds. No alkylidene minimum with the methylene ligand occupying the axial position was found on the reaction surface.

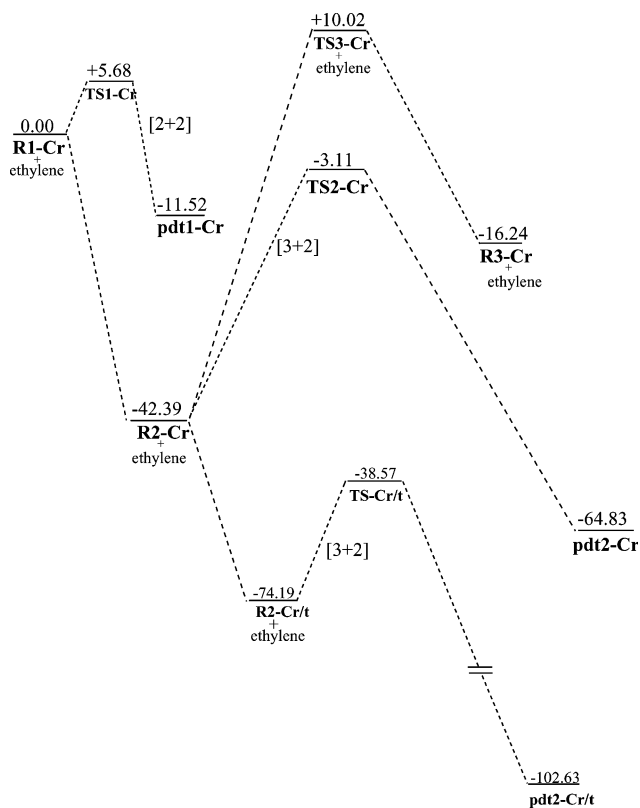


Fig. 2 Energetics of the reactions of Cl_4CrCH_2 with ethylene (t = triplet state). Relative energies in kcal mol^{-1} .

The carbenoid **R2-Cr** complex is 42.39 kcal mol^{-1} more stable than the carbene complex **R1-Cr** and 26.66 kcal mol^{-1} more stable than the bridged complex **R3-Cr**. It is found that **R2-Cr** can be transformed to **R3-Cr** through transition state **TS3-Cr**, but this conversion, which has an activation barrier of 44.66 kcal mol^{-1} , is not competitive with the formation of **pdt2-Cr** from **R2-Cr**, a reaction which requires an activation energy of 31.53 kcal mol^{-1} (*vide infra*).

The reactant **R1-Cr** could not be located on the triplet and quartet PESs while an open-shell singlet carbene complex located

turned out to be an exact replica of the closed-shell **R1-Cr** in terms of geometry and energy. A triplet carbenoid (**R2-Cr/t**) was found to be 31.80 kcal mol^{-1} more stable than the singlet carbenoid **R2-Cr**.

A search for a Cr carbene-ethylene π -bonded complex on the reaction surface yielded no stationary point while a singlet π -bonded complex (**p1-Cr**) optimized from the interaction of the carbenoid and ethylene is 2.13 kcal mol^{-1} less stable than the separated carbenoid (**R2-Cr**) and ethylene reactants, but 32.51 kcal mol^{-1} more stable than the separated carbene (**R1-Cr**) and ethylene reactants. The triplet state **p1-Cr** was found to be 32.15 kcal mol^{-1} more stable than the singlet state **p1-Cr**.

The formation of the metallacyclobutane **pdt1-Cr** through the transition state **TS1-Cr** by [2+2] addition of ethylene across the Cr–C bond of the carbene complex **R1-Cr** is 11.52 kcal mol^{-1} exothermic and has an activation barrier of 5.68 kcal mol^{-1} (Fig. 2). The metallacyclobutane **pdt1-Cr** formed is symmetric with respect to the Cr–C and C–C bonds, and has a Cr–C–C dihedral angle of 6.88°. This places the two Cr–C bonds in almost the same plane. The Cr=C bond increases from 1.756 Å in the reactant (**R1-Cr**) to 1.820 Å in the transition state (**TS1-Cr**) while the ethylene C=C bond increases from 1.331 Å in the reactant olefin to 1.380 Å in the transition state. In transition state **TS1-Cr**, the Cr–C–C dihedral angle is 9.22°, giving the four reacting atoms an almost planar four-center geometry which is typical for olefin insertion into M–C σ bonds.^{45–47} Triplet state structures for transition state **TS1-Cr** and product **pdt1-Cr** were found not to exist on the reaction surface, while an open-shell singlet **pdt1-Cr** which was found turned out to be the same as the closed-shell singlet **pdt1-Cr** with regard to its energy and geometry.

The [3+2] addition of ethylene across the Cr–C and Cr–Cl bonds of Cl_4CrCH_2 does not seem to proceed from the carbene reactant since no transition state was located for this reaction step. The process does however proceed from the carbenoid. The addition across the carbenoid complex **R2-Cr** through transition state **TS2-Cr** leads to a product **pdt2-Cr** in which the Cl atom is transferred from the metal center to the terminal carbon atom. This reaction has an activation barrier of 39.28 kcal mol^{-1} and the resulting product (**pdt2-Cr**) is 64.83 kcal mol^{-1} exothermic; 53.31 and 48.59 kcal mol^{-1} more stable than the metallacyclobutane **pdt1-Cr** and the chlorine-bridged complex **R3-Cr**, respectively. On the triplet PES, the activation barrier for the [3+2] addition of ethylene across the Cr–C and Cr–Cl bonds of the triplet carbenoid (**R2-Cr/t**) through triplet transition state **TS2-Cr/t** is 35.62 kcal mol^{-1} . The resulting triplet product (**pdt2-Cr/t**) is very stable (–102.63 kcal mol^{-1}), making it the global minimum on the portions of the reaction surface explored.

A transition state linking the carbenoid **R2-Cr** or the carbenoid-ethylene π -complex **p1-Cr** to the metallacyclobutane product **pdt1-Cr** could not be located on the reaction surface, probably suggesting that the formation of the metallacyclobutane, which is the first step of the olefin metathesis reaction according to the Herrison–Chauvin mechanism, may not proceed from the carbenoid complex. Thus the most likely active species for olefin metathesis in the Cr complex (if it is to occur) is the carbene complex $\text{Cl}_4\text{Cr}=\text{CH}_2$. Even though Fig. 2 shows that the [2+2] addition of ethylene across the Cr–C bond of $\text{Cl}_4\text{Cr}=\text{CH}_2$ to form the metallacyclobutane intermediate **pdt1-Cr** has a lower activation barrier than the [3+2] addition pathway, olefin metathesis

Table 1 Calculated relative energies (in kcal mol⁻¹) of the main stationary points for the [2+2] and [3+2] addition of Cl₄MCH₂ (M = Cr, Mo, W, Ru, Re) complexes to ethylene^a

complex	carbene + olefin	carbenoid + olefin	TS[2+2]	TS[3+2]	pdt[2+2]	pdt[3+2]
Cl ₄ CrCH ₂	0.00	-42.39	+5.68	-3.11 ^b	-11.52	-64.83
Cl ₄ MoCH ₂	0.00	+7.68	+5.33	+6.91	-12.26	-26.77
Cl ₄ WCH ₂	0.00	+31.23	+2.93	+13.65	-13.31	-5.32
Cl ₄ RuCH ₂	0.00	-33.40	+0.48	-4.02 ^b	-16.76	-65.54
Cl ₄ ReCH ₂ ^c	0.00	+5.15	+2.58	+6.64	-13.74	-27.77

^a Energies calculated relative to the respective separated carbene and ethylene reactants. ^b In Cl₄CrCH₂ and Cl₄RuCH₂ the [3+2] addition pathway involves the carbenoid complex and not the carbene complex. Thus the activation barrier for [3+2] addition in these complexes are 31.53 and 29.38 kcal mol⁻¹ respectively. ^c The Re complex has a doublet ground state electronic structure.

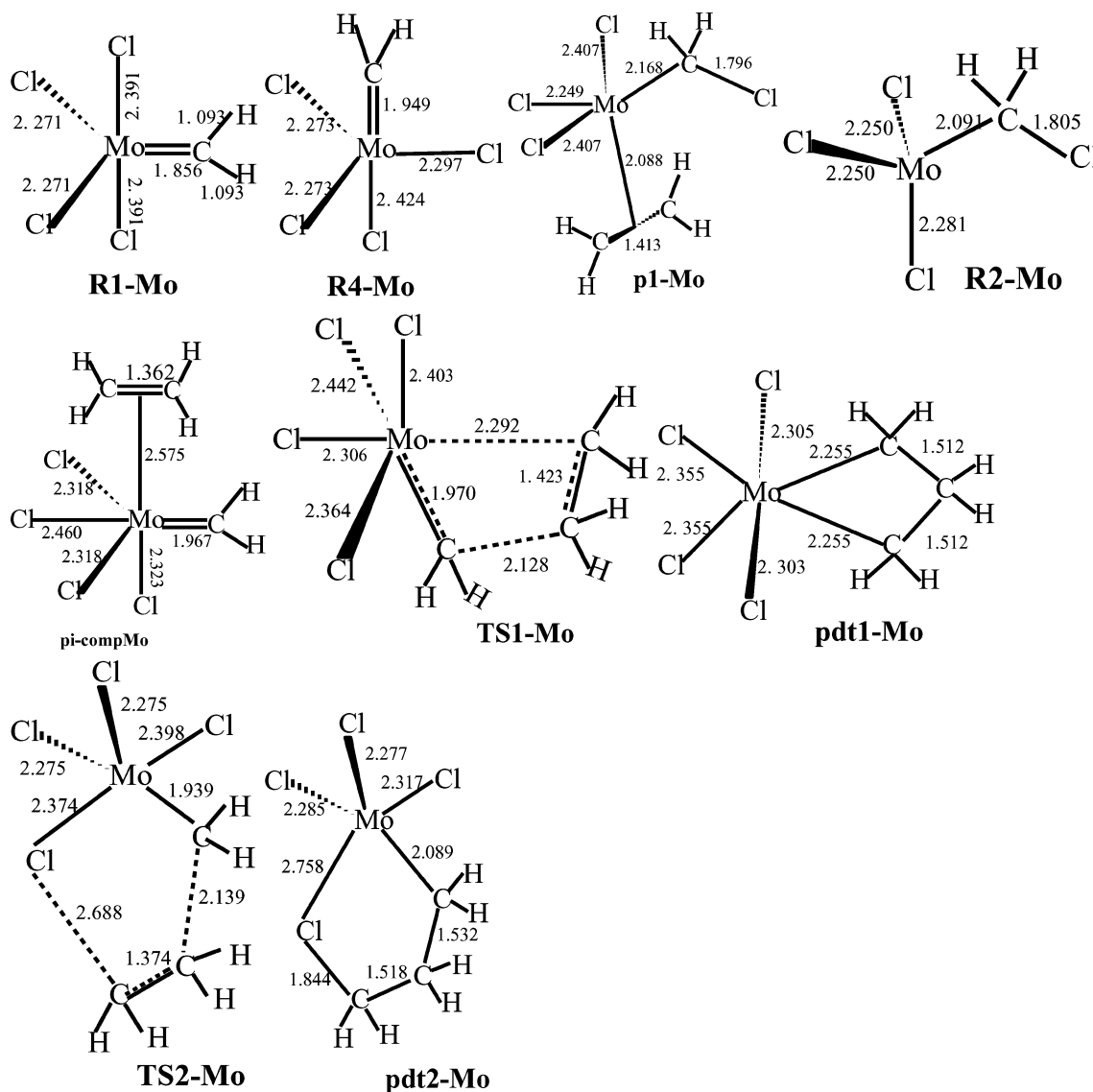


Fig. 3 Optimized geometries of the main stationary points involved in the reaction of Cl₄MoCH₂ with ethylene. Distances in Å and angles in degrees.

is not likely to occur with the Cl₄CrCH₂ complex because the existence of a lower-energy carbenoid Cl₃CrCH₂Cl complex (**R2-Cr** and **R2-Cr/t**) will most likely deplete the reaction surface of the active carbene species **R1-Cr** for the process (*vide supra*). This is consistent with the fact that no olefin metathesis reaction has been reported with Cr complexes of this nature to date.

Table 1 gives a summary of the relative energies of the main stationary points involved in the reaction of Cl₄MCH₂ (M = Cr, Mo, W, Ru, Re) complexes with ethylene.

The optimized geometries and relative energies of the main stationary points involved in the reaction of Cl₄MoCH₂ with ethylene are shown in Fig. 3 and Fig. 4, respectively. A geometry

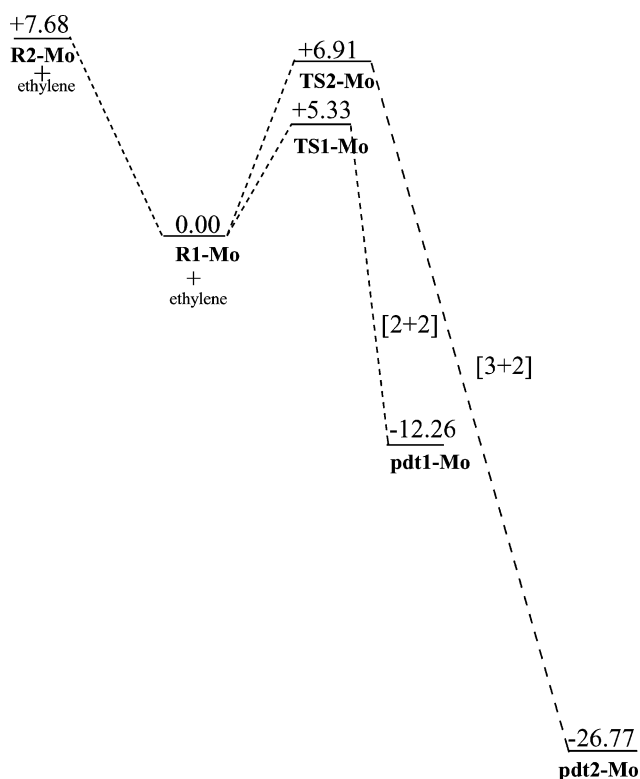


Fig. 4 Energetics of the reactions of Cl_4MoCH_2 with ethylene. Relative energies in kcal mol^{-1} .

optimization of the Mo complex Cl_4MoCH_2 on the closed-shell singlet PES yielded two trigonal bipyramidal carbene conformers: one in which the CH_2 ligand is in the axial position (**R4-Mo**) and the other in which the methylene ligand occupies the equatorial position (**R1-Mo**). A third minimum has been located on the reaction surface corresponding to a carbenoid $\text{Cl}_3\text{MoCH}_2\text{-Cl}$ species (**R2-Mo**). The equatorial carbene **R1-Mo** is $12.89 \text{ kcal mol}^{-1}$ more stable than the axial carbene **R4-Mo** and $7.68 \text{ kcal mol}^{-1}$ more stable than the carbenoid complex **R2-Mo**. The axial Mo–Cl bonds are $0.12\text{--}0.15 \text{ \AA}$ longer than the corresponding equatorial bonds. The triplet state **R1-Mo** has been found to be $11.60 \text{ kcal mol}^{-1}$ less stable than the singlet reactant while the open-shell singlet structure located is the exact replica of the closed-shell singlet structure. The triplet carbenoid is $28.00 \text{ kcal mol}^{-1}$ more stable than the triplet carbene.

A carbene–ethylene π -bonded complex (**pi-compMo**) optimized from the interaction of the equatorial conformer of the carbene complex with ethylene is found to be $5.66 \text{ kcal mol}^{-1}$ less stable than the separated reactants. The singlet π -complex **p1-Mo** obtained from the interaction of the carbenoid (**R2-Mo**) and ethylene is $22.67 \text{ kcal mol}^{-1}$ more stable than the separated carbenoid and ethylene reactants and $14.99 \text{ kcal mol}^{-1}$ more stable than the carbene and ethylene reactants. The triplet state **p1-Mo** is $0.20 \text{ kcal mol}^{-1}$ less stable than the separated triplet carbenoid and ethylene reactants. The Mo–C bond is 0.164 \AA longer in the triplet carbene than the singlet carbene.

The formation of metallacyclobutane **pdt1-Mo** through transition state **TS1-Mo** by [2+2] addition of ethylene across the Mo–C bond of the carbenic Cl_4MoCH_2 (**R1-Mo**) has an activation barrier of $5.33 \text{ kcal mol}^{-1}$ and exothermicity of $12.26 \text{ kcal mol}^{-1}$.

The geometries of the Mo metallacyclobutane intermediate and transition state are very similar to the geometries of the corresponding structures in the Cr complex. The metallacyclobutane is symmetric with respect to the Mo–C and C–C bonds. In transition state **TS1-Mo** the Mo–C–C–C dihedral angle is 4.39° , giving the four reacting atoms an almost planar four-center geometry. However, in the metallacyclobutane **pdt1-Mo** the four-membered ring is distorted out of plane by 12.54° compared to the Cr metallacyclobutane **pdt1-Cr**. The exothermicity of the Mo and Cr products is also comparable; the Mo metallacyclobutane complex is just $0.74 \text{ kcal mol}^{-1}$ more stable than the Cr complex.

On the triplet PES, the **pdt1-Mo** is $30.23 \text{ kcal mol}^{-1}$ exothermic; $17.97 \text{ kcal mol}^{-1}$ more exothermic than the singlet **pdt1-Mo**. The triplet transition state for the formation of **pdt1-Mo** is $12.43 \text{ kcal mol}^{-1}$ above the singlet reactants and $0.83 \text{ kcal mol}^{-1}$ above the triplet reactants. The two Mo–C bonds of the triplet metallacyclobutane are 0.297 \AA longer than those of the singlet species while the Mo–C–C–C dihedral angle in the triplet product is 9.6° compared to the angle of 16.93° in the singlet species. Thus the triplet metallacyclobutane ring is more planar than the singlet species.

A [3+2] addition of ethylene across the Mo–C and Mo–Cl bonds of the singlet carbene complex **R1-Mo** leading to the singlet product **pdt2-Mo**, which is $26.77 \text{ kcal mol}^{-1}$ exothermic, has an activation barrier of $6.91 \text{ kcal mol}^{-1}$ through the singlet transition state **TS2-Mo**. The triplet **pdt2-Mo** has been found to be $21.95 \text{ kcal mol}^{-1}$ more stable than the singlet **pdt2-Mo**. The triplet transition state **TS2-Mo** is not found on the reaction surface.

The olefin metathesis reaction in Mo is not likely to proceed from the carbenoid complex **R2-Mo** or the carbenoid π -complex **p1-Mo** since a transition state linking the carbenoid complex and metallacyclobutane product could not be located. Thus the most likely active species for the olefin metathesis is the carbene complex $\text{Cl}_4\text{Mo}=\text{CH}_2$. As Fig. 4 and Table 1 show the [2+2] addition pathway is favored over the [3+2] route in terms of activation barriers, indicating that olefin metathesis will most likely occur in the Mo system. However, the kinetic preference of the [2+2] pathway is only marginal and, given the much higher exothermicity of the [3+2] route, the [3+2] addition pathway is likely to be competitive with the [2+2] addition route. If the barriers for the formation of **p1-Mo**, which could not be determined in this work, turns out to be favorable and **p1-Mo** becomes accessible in the reaction mixture, then the population of the active species will decrease as a result since **p1-Mo** is more stable than the separated carbene and ethylene. This might decrease the activity of the Mo catalyst in the olefin metathesis reaction.

The optimized geometries and relative energies of the main stationary points involved in the reaction of Cl_4WCH_2 with ethylene are shown in Fig. 5 and Fig. 6 respectively. On the singlet tungsten reaction surface, two carbene complex minima are located: an equatorial conformer (**R1-W**) and an axial conformer (**R4-W**). The equatorial conformer is $13.36 \text{ kcal mol}^{-1}$ more stable than the axial conformer. The W=C bond is marginally shorter (by 0.072 \AA) in the equatorial carbene conformer than in the axial conformer. The triplet state **R1-W** is $19.52 \text{ kcal mol}^{-1}$ less stable than the singlet species and the W–C bond is 0.109 \AA longer in the triplet carbene than in the singlet carbene. A carbenoid minimum (**R2-W**) is also located on the surface but is 31.23 kcal

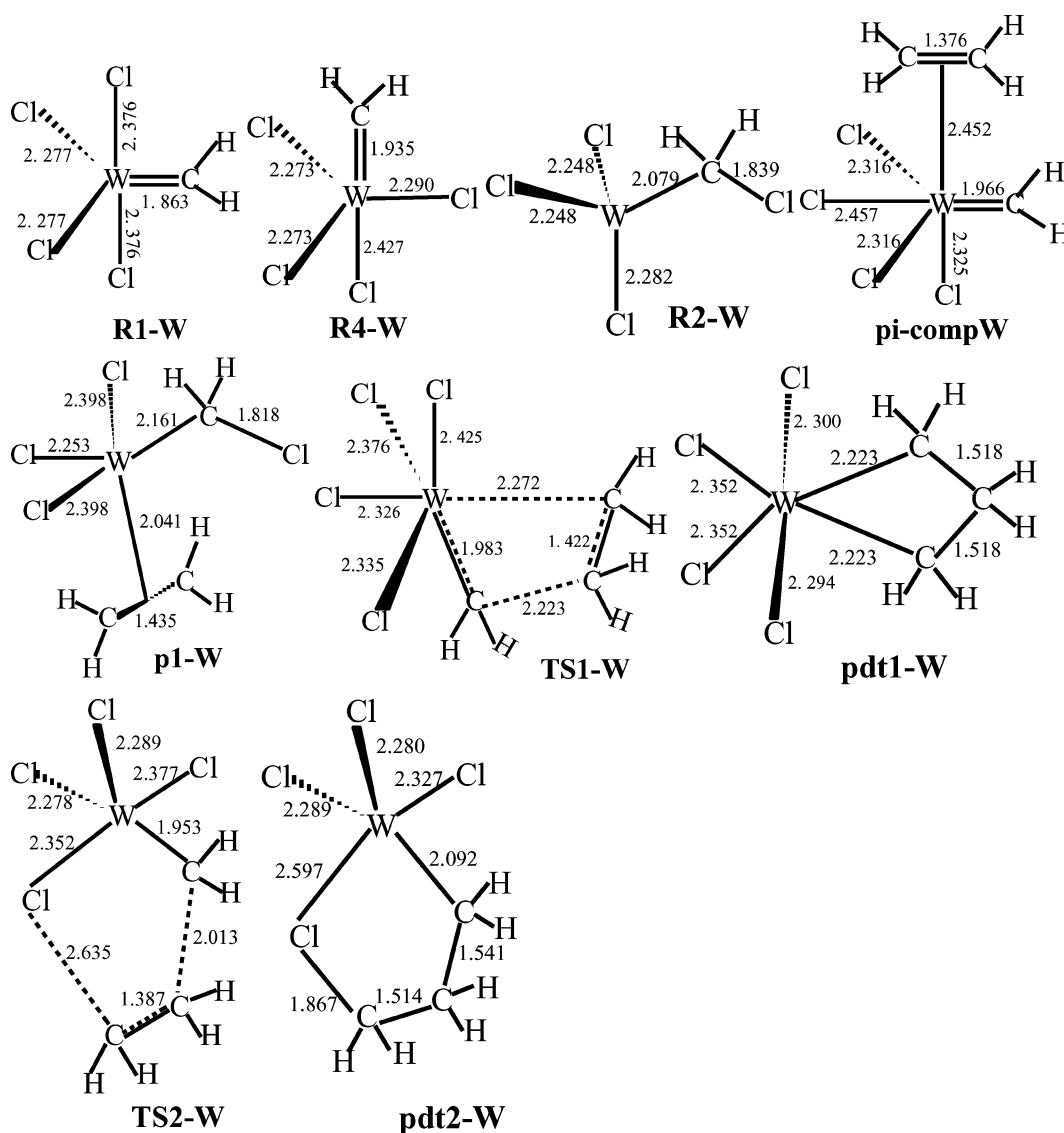


Fig. 5 Optimized geometries of the main stationary points involved in the reaction of Cl_4WCH_2 with ethylene. Distances in Å and angles in degrees.

mol^{-1} and $17.89 \text{ kcal mol}^{-1}$ less stable than the equatorial and axial carbene complexes, respectively. The C–Cl bond in the tungsten carbenoid **R2-W** is 0.034 and 0.064 Å longer than that in the Mo carbenoid (**R2-Mo**) and Cr carbenoid (**R2-Cr**), respectively. The bond lengths for the W axial and equatorial carbene complexes (**R1-W** and **R4-W**) are systematically shorter by between 0.094 and 0.253 Å compared to those reported by Sodupe *et al.*⁴⁸ in an *ab initio* Hartree–Fock study of this system.

The π -complex (**pi-compW**) that has been optimized from the interaction between the equatorial carbene and ethylene is $9.44 \text{ kcal mol}^{-1}$ less stable than the separated reactants. The olefinic C–C bond is 0.014 Å longer in the W π -complex than in the Mo π -complex. The π -complex **p1-W** formed from the interaction of the carbenoid and ethylene is $34.79 \text{ kcal mol}^{-1}$ more stable than the carbenoid and ethylene reactants, and $3.56 \text{ kcal mol}^{-1}$ more stable than the carbene and ethylene reactants. It appears that the π -complex **p1-W** might be in equilibrium with the carbene and ethylene reactants. The triplet state π -complex **p1-W** is 9.94

kcal mol^{-1} less stable than the singlet species. The most likely active species for the olefin metathesis appears to be only the carbene complex $\text{Cl}_4\text{W}=\text{CH}_2$ and not the carbenoid since no transition state was located linking the carbenoid complex **R2-W** or the carbenoid π -complex **p1-W** and the metallacyclobutane intermediate.

The activation barrier for the [2+2] addition of ethylene across the W–C bond of the carbene complex through transition state **TS1-W** is $2.93 \text{ kcal mol}^{-1}$. The resultant metallacyclobutane **pdt1-W** is $13.31 \text{ kcal mol}^{-1}$ exothermic. This activation barrier is lower than that computed for the corresponding reactions in the Cr and Mo systems, while the formation of the W metallacyclobutane is slightly more exothermic than the formation of the Cr and Mo metallacyclobutanes. The metallacyclobutane is also symmetric with respect to the W–C and C–C bonds as is the case for the Cr and Mo species. The W–C–C–C dihedral angle of 3.08° in the transition state is distorted by 15.74° in the metallacyclobutane **pdt1-W**.

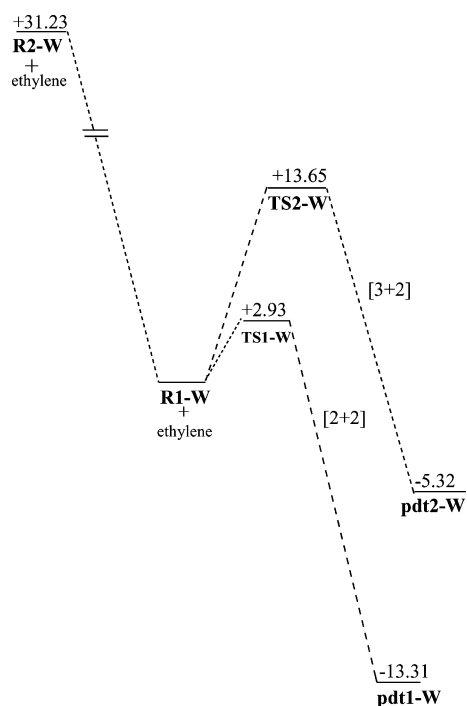


Fig. 6 Energetics of the reactions of Cl_4WCH_2 with ethylene. Relative energies in kcal mol^{-1} .

The triplet state transition state **TS1-W** is $17.89 \text{ kcal mol}^{-1}$ higher in energy than the singlet species. The newly-forming W–C bond is 0.291 \AA longer in the triplet transition state than in the singlet transition state while the newly-forming C–C bond is

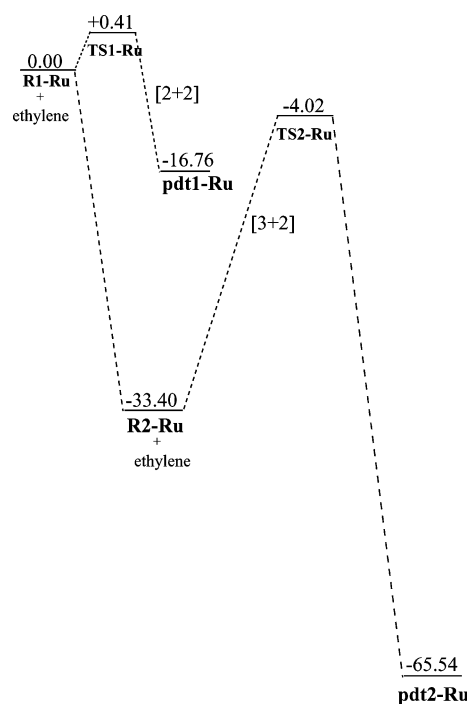


Fig. 8 Energetics of the reactions of Cl_4RuCH_2 with ethylene. Relative energies in kcal mol^{-1} .

marginally shorter (by 0.031 \AA) in the triplet species than in the singlet species. The resulting triplet metallacycle is $17.73 \text{ kcal mol}^{-1}$ less stable than the singlet **pdt1-W**. With a W–C–C–C dihedral angle of 0.88° , the triplet metallacycle ring is much more planar

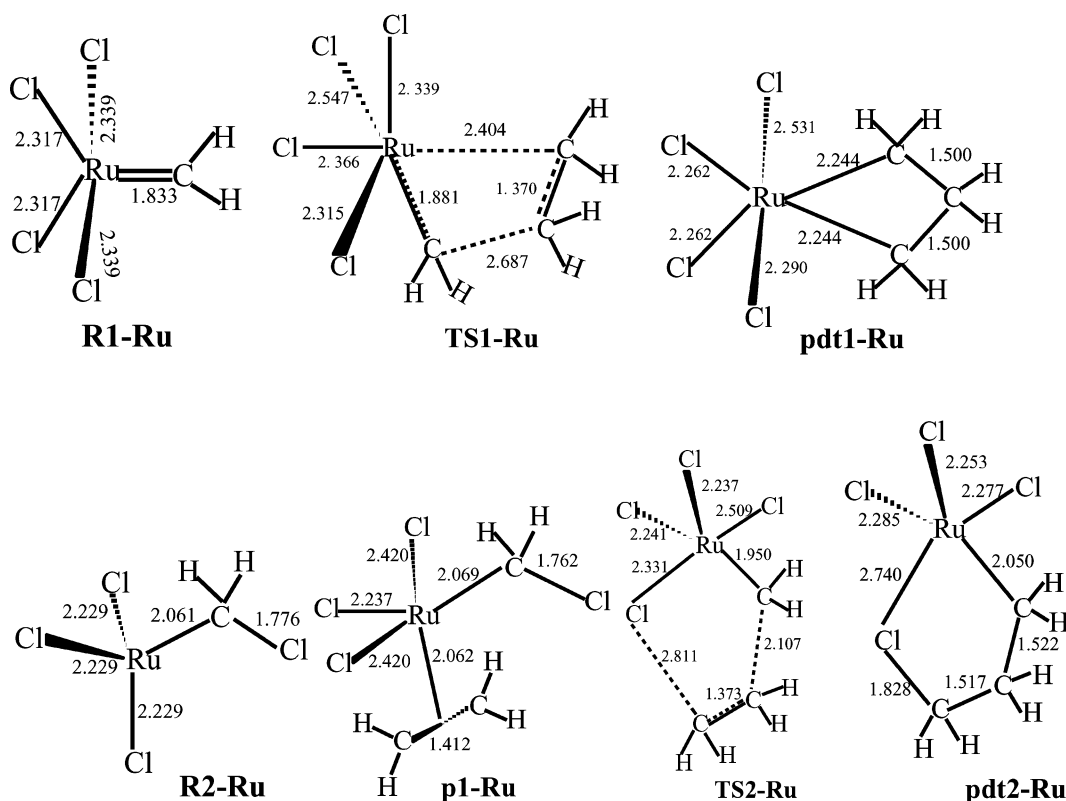


Fig. 7 Optimized geometries of the main stationary points involved in the reaction of Cl_4RuCH_2 with ethylene. Distances in \AA and angles in degrees.

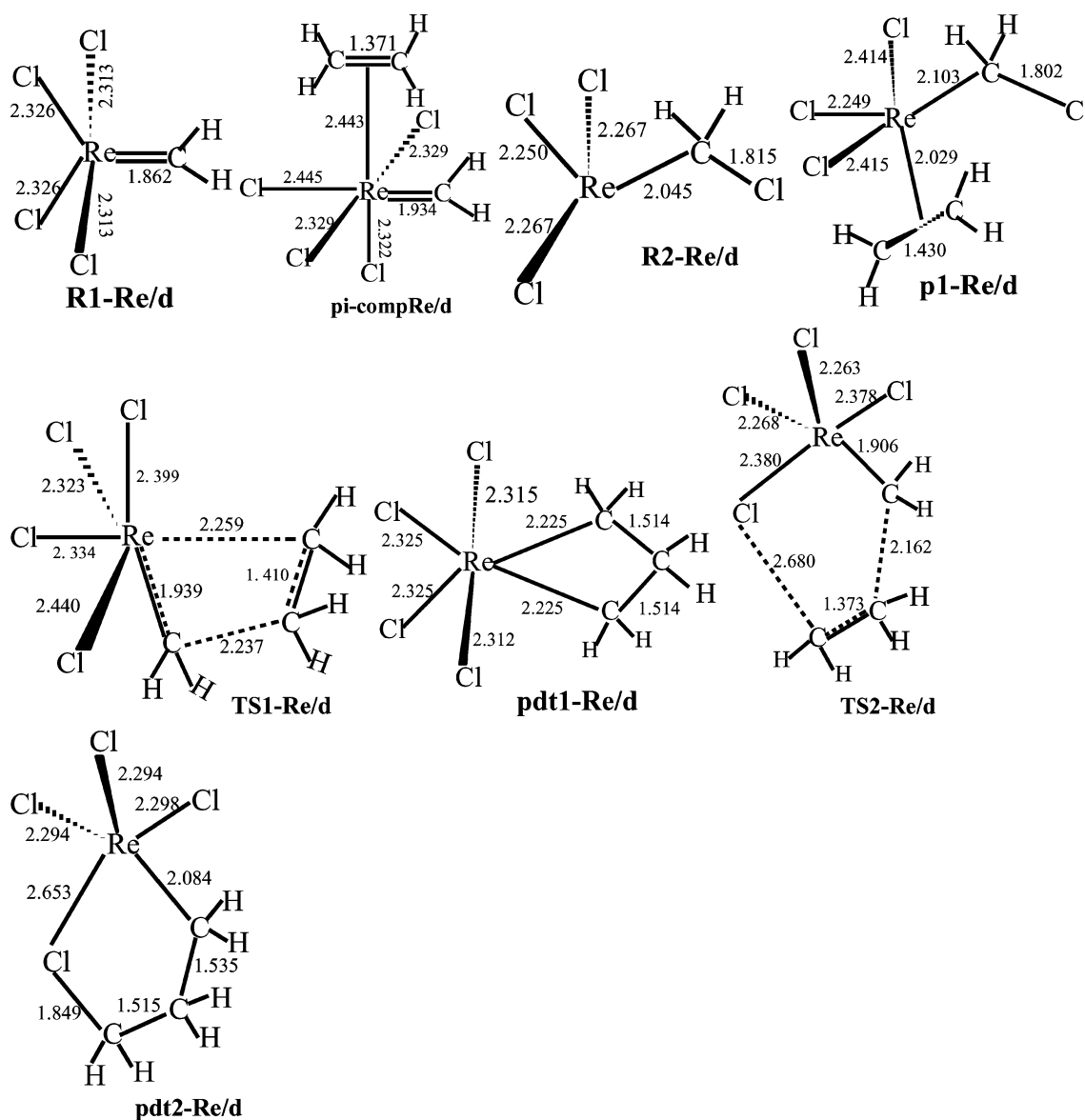


Fig. 9 Optimized geometries of the main stationary points involved in the reaction of Cl_4ReCH_2 with ethylene. Distances in Å and angles in degrees.

than the singlet metallacycle. An open-shell singlet **pdt1-W** turns out to be exactly like the closed-shell singlet species in terms of energy and geometry.

Along the [3+2] addition pathway, ethylene adds across the W–C and W–Cl bonds of the carbene complex through transition state **TS2-W**, with a barrier of 13.65 kcal mol⁻¹, to form species **pdt2-W** which is 5.32 kcal mol⁻¹ exothermic on the singlet PES and 22.98 kcal mol⁻¹ exothermic on the triplet PES, the W–Cl forming bond being 0.174 Å longer in the triplet structure than in the singlet structure. Thus the [2+2] addition reaction pathway to form the metallacyclobutanes is more favorable, kinetically and thermodynamically, than the [3+2] addition reaction pathway and therefore the W complex should be able to catalyze metathesis. The energetic preference of the [2+2] over the [3+2] pathway is unambiguous in the W system, unlike in the Mo system where the [3+2] pathway is likely to be competitive with the [2+2] pathway. Also there is no low-energy carbenoid reaction path that might

compete with the metathesis process. These results are consistent with earlier suggestions that the W alkylidene catalyst has a greater metathesis activity than the Mo species.²⁸ A Mulliken population analysis of the carbene complexes reveals that the order of polarization of the M–C bond in a $\text{M}^+=\text{C}^-$ fashion is in the order: $\text{W} > \text{Mo} > \text{Cr}$. This observation supports the finding by Cundari and Gordon²⁸ that the W–C bond is more polarized than the Mo–C bond in the methyldene complexes. The extent of polarization has been found to be comparable in the Mo and W carbenoid complexes.

The optimized geometries and relative energies of the main stationary points involved in the reaction of Cl_4RuCH_2 with ethylene are shown in Fig. 7 and Fig. 8 respectively. On the singlet Ru reaction surface an equatorial carbene conformer $\text{Cl}_4\text{Ru}=\text{CH}_2$ structure (**R1-Ru**) and a carbenoid $\text{Cl}_3\text{RuCH}_2\text{-Cl}$ structure (**R2-Ru**) are located. The carbenoid complex is 33.46 kcal mol⁻¹ more stable than the carbene complex. In contrast, DFT

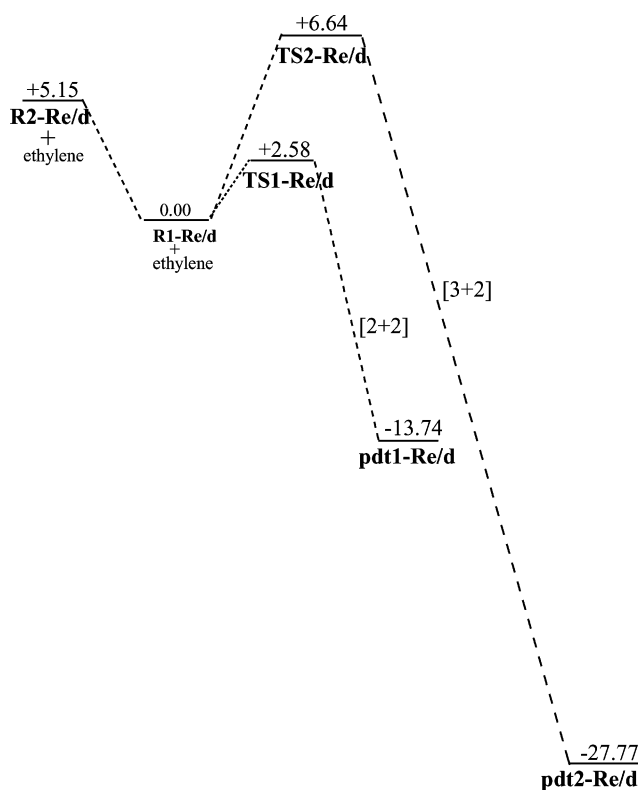


Fig. 10 Energetics of the reactions of Cl_4ReCH_2 with ethylene. Relative energies in kcal mol^{-1} .

B3LYP studies by Bernardi *et al.*³⁶ on olefin metathesis catalyzed by Grubbs ruthenium complexes found the equatorial carbenic complex $\text{Cl}_2(\text{PH}_3)_2\text{Ru}=\text{CH}_2$ to be $18.45 \text{ kcal mol}^{-1}$ more stable than the carbenoid $\text{Cl}_2(\text{PH}_3)\text{RuCH}_2(\text{PH}_3)$ species. The triplet carbene complex has been found to be $12.77 \text{ kcal mol}^{-1}$ more stable than the singlet carbene while the triplet carbenoid is $0.86 \text{ kcal mol}^{-1}$ less stable than the singlet carbenoid.

The axial carbene conformer and a carbene–ethylene π -bonded complex could not be located on the reaction surface. An ethylene π -bonded carbenoid complex **p1-Ru** optimized from the interaction of the carbenoid and ethylene has been found to be $6.74 \text{ kcal mol}^{-1}$ more stable than the separated singlet carbenoid and ethylene reactants, and $40.16 \text{ kcal mol}^{-1}$ more stable than the separated carbene and ethylene reactants. The triplet carbenoid–ethylene π -complex is $2.68 \text{ kcal mol}^{-1}$ more stable than the singlet π -complex. The distance between the Ru center and the olefinic C–C centroid is 0.330 \AA longer in the triplet π -complex than in the singlet π -complex.

The activation barrier through transition state **TS1-Ru** for the [2+2] addition of ethylene across the Ru–C bond of the carbene is $0.48 \text{ kcal mol}^{-1}$, which is smaller than the barriers of 9.7 and $9.6 \text{ kcal mol}^{-1}$ for norbornene and 1-butene respectively found by Cavallo³⁵ in the study of the mechanism of metathesis reactions of 1-butene and norbornene catalyzed by model Grubbs Ru catalysts. The resultant metallacyclobutane intermediate **pdt1-Ru** (Fig. 7 and Fig. 8), which is $16.76 \text{ kcal mol}^{-1}$ exothermic, is symmetric with respect to the Ru–C and C–C bonds. The Ru–C–C–C dihedral angle is 5.50° in transition state **TS1-Ru** and 5.54° in the metallacyclobutane **pdt1-Ru**. Thus there is no

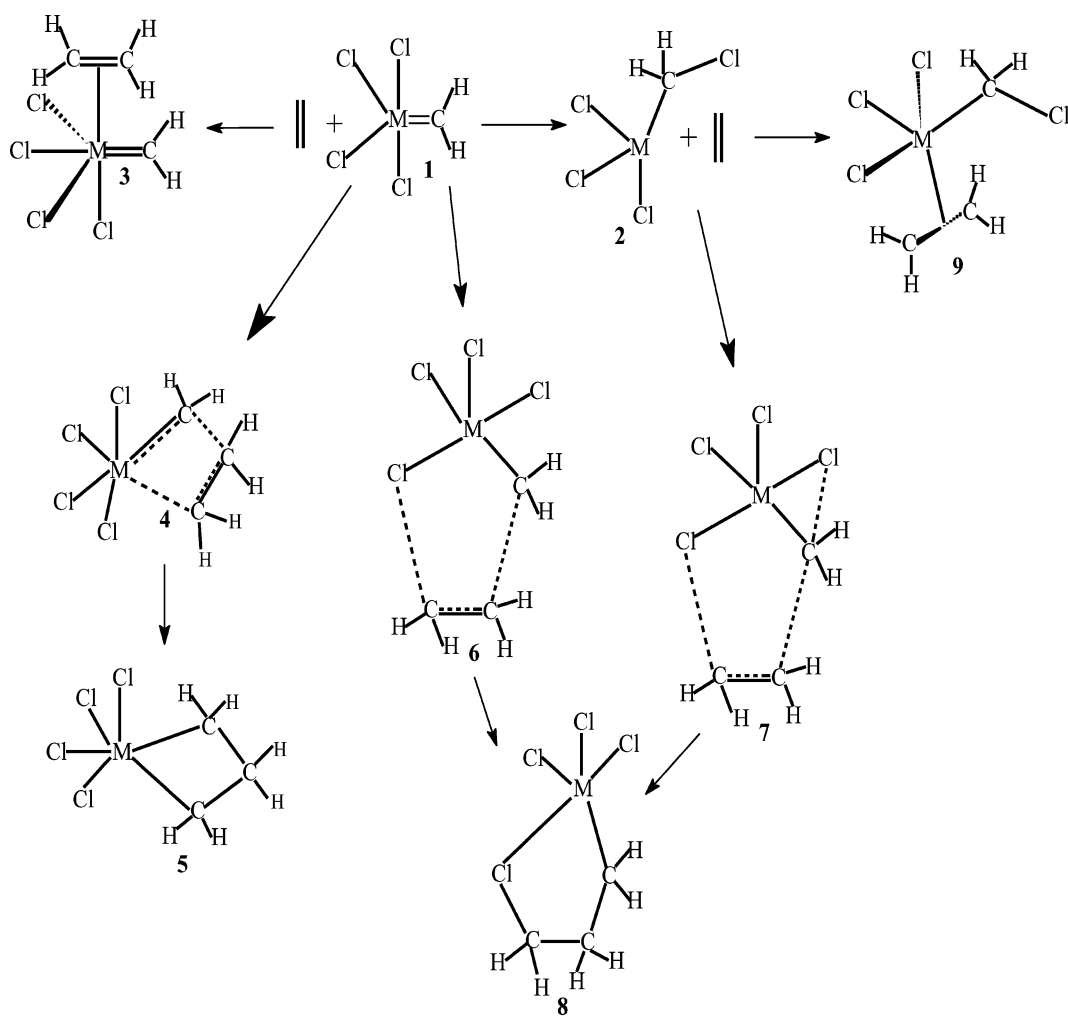
considerable distortion of the planar geometry of the forming ring during the formation of the metallacyclobutane from the transition state. The activation barrier for the [2+2] addition of ethylene across the Ru–C bond of triplet carbene through a triplet transition state **TS1-Ru/t** is $3.58 \text{ kcal mol}^{-1}$. The newly-forming Ru–C and C–C bonds are 0.317 \AA and 0.639 \AA , respectively, longer in the triplet transition state than in the singlet transition state.

Just as was observed for the Cr complex, the [3+2] addition of ethylene across the Ru–C and Ru–Cl bonds of Cl_4RuCH_2 does not appear to proceed from the carbene complex but rather from the carbenoid. The [3+2] addition of ethylene across the Ru–C and Ru–Cl bonds of carbenoid **R2-Ru** through transition state **TS2-Ru** has a barrier of $29.38 \text{ kcal mol}^{-1}$, leading to a very exothermic ($-65.54 \text{ kcal mol}^{-1}$) product **pdt2-Ru**.

It has been concluded that a metallacyclobutane may not originate from the carbenoid complex, since no transition state was located linking the carbenoid and the metallacycle. Thus the active species for olefin metathesis in the Ru complex (if it is to occur) should be the carbene complex. The work of Bernardi *et al.*³⁶ has also found the metal carbene complex $(\text{PH}_3)_2\text{Ru}=\text{CH}_2$ to be the “primary” active catalytic species. However, they also found out that the carbenoid complexes would represent “secondary” active species for the formation of a metallacyclobutane intermediate. The present study also agrees with the work of Bernardi *et al.*³⁶ and Grubbs *et al.*^{32,33} that the metallacyclobutane is an intermediate and not a transition state. Even though the [2+2] addition of ethylene across the carbene which leads to the formation of the metallacyclobutane **pdt1-Ru** has a very low activation barrier (Table 1 and Fig. 8), the reaction surface is likely to be populated by the carbenoid complex reactant **R2-Ru** and not the carbene complex **R1-Ru**. Thus the formation of **pdt1-Ru**, which will ultimately lead to olefin metathesis, may not occur since the reaction surface may be depleted of the active species for metathesis.

The optimized geometries and relative energies of the main stationary points involved in the reaction of Cl_4ReCH_2 with ethylene are shown in Fig. 9 and Fig. 10, respectively. No stationary points could be located on the singlet and triplet PESs respectively. The reactant minima **R1-Re/d** and **R1-Re/q** were located on the doublet and quartet PESs; the doublet structure being $12.40 \text{ kcal mol}^{-1}$ more stable than the quartet structure. The Re–C double bond is 0.112 \AA longer in the quartet species than in the doublet species. The carbenoid species **R2-Re/d** located on the doublet surface is $5.15 \text{ kcal mol}^{-1}$ less stable than the doublet carbene while the quartet carbenoid located is $2.93 \text{ kcal mol}^{-1}$ more stable than the doublet carbene. π -complexation of the doublet and quartet carbenoids with ethylene stabilizes the system by 21.55 and $8.49 \text{ kcal mol}^{-1}$ respectively relative to the separated reactants. This contrasts with π -complexation of the doublet carbene with ethylene which destabilizes the system by only $1.11 \text{ kcal mol}^{-1}$ relative to the separated reactants.

The doublet transition state **TS1-Re/d** that connects the carbene reactant **R1-Re/d** to the doublet product **pdt1-Re/d** in the [2+2] addition of ethylene across the Re–C bond of Cl_4ReCH_2 is $2.58 \text{ kcal mol}^{-1}$ above the doublet carbene and ethylene reactants on the potential energy profile. The product **pdt1-Re/d** resulting from this addition is $13.74 \text{ kcal mol}^{-1}$ exothermic. The Re–C–C₁–C₂ dihedral angle (where C₁ and C₂ are the olefinic carbons) of 4.52°



reaction route	metal complex
$1 \rightarrow 4 \rightarrow 5^a$	Cr, Mo, W, Ru, Re
$1 \rightarrow 6 \rightarrow 8$	Mo, W, Re
$2 \rightarrow 7 \rightarrow 8^b$	Cr, Ru
$1 \rightarrow 3$	Mo, W, Ru, Re
$2 \rightarrow 9$	Cr, Mo, W, Ru, Re

^a $1 \rightarrow 4 \rightarrow 5$ is preferred route in Mo, W, Re

^b $2 \rightarrow 7 \rightarrow 8$ is preferred route in Cr, Ru

Fig. 11 Summary of the possible reaction paths for the reaction of Cl_4MCH_2 ($\text{M} = \text{Cr, Mo, W, Ru, Re}$) with ethylene.

in transition state **TS1-Re/d** increases to 14.15° in the product **pdt1-Re/d**.

The activation barrier for the [3+2] addition of ethylene across the Re–Cl and Re–C bonds of doublet Cl_4ReCH_2 through the doublet transition state **TS2-Re/d** is $6.64 \text{ kcal mol}^{-1}$. The product formed, which is also a doublet species, is $27.77 \text{ kcal mol}^{-1}$

exothermic. No quartet state **TS1-Re** and **TS2-Re** were located on the PESs.

Since the activation barrier of the formation of the metallacyclobutane **pdt1-Re** is lower than the barrier for the formation of product of [3+2] addition **pdt2-Re**, the Re complex is likely to catalyze metathesis.

Fig. 11 is a summary of the possible paths for the reactions of the complexes Cl_4MCH_2 ($\text{M} = \text{Cr, Mo, W, Ru, Re}$) with ethylene. The Mo, W, and Re complexes can follow two reaction paths: $1 \rightarrow 4 \rightarrow 5$ and $1 \rightarrow 6 \rightarrow 8$, but the former route is preferred over the latter. The preference for the $1 \rightarrow 4 \rightarrow 5$ route over $1 \rightarrow 6 \rightarrow 8$ is clearly unambiguous in W, whereas in Mo the latter route is likely to be competitive with the former. The Cr and Ru complexes can also follow paths: $1 \rightarrow 4 \rightarrow 5$ and $2 \rightarrow 7 \rightarrow 8$, but the latter path is preferred over the former.

Conclusions

Table 1 indicates that the reaction of $\text{Cl}_4\text{M}=\text{CH}_2$ with ethylene to form a metallacyclobutane is a low-barrier process for each of the metal complexes studied, the highest barrier being $5.68 \text{ kcal mol}^{-1}$ for the Cr complex and the lowest being $0.48 \text{ kcal mol}^{-1}$ for the Ru complex. The activation barriers of the complexes studied were found to decrease in the order: $\text{Cr} > \text{Mo} > \text{W} \approx \text{Re} > \text{Ru}$ while the exothermicities decrease in the order: $\text{Ru} (16.76 \text{ kcal mol}^{-1}) > \text{Re} \approx \text{W} > \text{Mo} > \text{Cr} (11.52 \text{ kcal mol}^{-1})$.

Attempts at locating a transition state linking the metallacyclobutane product and the carbenoids in each of the systems studied yielded no stationary point, probably indicating that the formation of the metallacyclobutane is not likely to proceed from the carbenoid complexes. Therefore the active species for the metathesis reaction in each of these complexes are probably not carbenoids, but carbenes.

One key factor has been found to be responsible for the difference in metathesis activity in the complexes studied: the stability of the carbenoid complexes compared to the carbenes. In Cr and Ru, the carbenoid complexes are more stable than the carbenes and thus Cl_4CrCH_2 and Cl_4RuCH_2 are likely to exist in the lower-energy carbenoid $\text{Cl}_3\text{MCH}_2\text{Cl}$ form as opposed to the carbene $\text{Cl}_4\text{M}=\text{CH}_2$ form. This is likely to deplete the reaction surface of the active species of the process, making Cl_4MCH_2 ($\text{M} = \text{Cr, Ru}$) not suitable for olefin metathesis. This suggests that whereas Cl_4MCH_2 ($\text{M} = \text{Mo, W, Re}$) may catalyze olefin metathesis, Cl_4MCH_2 ($\text{M} = \text{Cr, Ru}$) may not. The kinetic and thermodynamic preference of the [2+2] pathway over the [3+2] pathway is unambiguous in $\text{Cl}_4\text{W}=\text{CH}_2$ whereas in Cl_4MoCH_2 the [3+2] pathway and the formation of carbenoid complexes may be competitive with the [2+2] pathway. The activation barrier of metallacyclobutane formation also indicates that the W and Re complexes may have a greater metathesis activity than the Mo complex.

The Cr and Ru carbene complexes do not seem to form π -complexes while the carbene–ethylene π -complexes located for Mo, W and Re are all higher-energy species relative to the reactants. The formation of the metallacyclobutanes does not appear to involve the prior formation of ethylene-bound π -complex. This must be considered in relation to the well-known difficulties for DFT methods to describe weak interactions.^{49–53} The B3LYP functional in particular does not describe dispersion, and therefore underestimate the interaction energies of π -bonded systems. This may well result in a repulsive interaction.^{54,55} Given these difficulties, it is difficult to assess the role of the π -complex in the mechanism of the reactions.

Some of the minima and transition states located in this work display multiple spin ground states. For the Cr and Ru complexes,

inclusion of the triplet state structures increases the stability of the carbenoid relative to the carbenes and this worsens the inability of the Cl_4CrCH_2 to catalyze metathesis. For the Re complex, the doublet ground state is more favored over the quartet ground state. The Re complex appears not to have a singlet or triplet ground state. Finally the reaction patterns of the Cr and Ru complexes are similar while those of the Mo and W are also similar.

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