PAPER

A density functional theory study of the mechanisms of oxidation of ethylene by rhenium oxide complexes†

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The oxo complexes of group VII B are of great interest for their potential toward epoxidation and dihydroxylation. In this work, the mechanisms of oxidation of ethylene by rhenium-oxo complexes of the type $LReO_3$ (L = O^-, Cl, CH_3, OCH_3, Cp, NPH_3) have been explored at the B3LYP/LACVP* level of theory. The activation barriers and reaction energies for the stepwise and concerted addition pathways involving multiple spin states have been computed. In the reaction of $LReO_3$ (L = O^-, Cl, CH_3, OCH_3, Cp, NPH_3) with ethylene, it was found that the concerted [3 + 2] addition pathway on the singlet potential energy surfaces leading to the formation of a dioxylate intermediate is favored over the [2 + 2] addition pathway leading to the formation of a metallaoxetane intermediate and its re-arrangement to form the dioxylate. The activation barrier for the formation of the dioxylate on the singlet PES for the ligands studied is found to follow the order $O^- > CH_3 > NPH_3 > CH_3O^- > Cl^- > Cp$ and the reaction energies follow the order $CH_3 > O^- > NPH_3 > CH_3O^- > Cl^- > Cp$. On the doublet PES, the [2 + 2] addition leading to the formation the metallaoxetane intermediate is favored over dioxylate formation for the ligands L = CH_3, CH_3O^-, Cl^-. The activation barriers for the formation of the metallaoxetane intermediate are found to increase for the ligands in the order $CH_3 < Cl^- < CH_3O^-$ while the reaction energies follow the order $Cl^- < CH_3O^- < CH_3$. The subsequent re-arrangement of the metallaoxetane intermediate to the dioxylate is only feasible in the case of $ReO_3(OCH_3)$. Of all the complexes studied, the best dioxylating catalyst is ReO_3Cp (singlet surface); the best epoxidation catalyst is ReO_3Cl (singlet surface); and the best metallaoxetane formation catalyst is $ReO_3(NPH_3)$ (triplet surface).

1. Introduction

The role of transition metal oxo compounds in the dihydroxylation of olefins is an important class of oxygen transfer reactions.[1–3] Many experimental and theoretical investigations have focused on mechanistic aspects of this type of reaction. Olefin dihydroxylation catalyzed by transition metal oxo species of the type LMO_3 has been the subject of extensive theoretical studies.[4–12]

In the initial step of the dihydroxylation reaction catalyzed by transition metal oxo compounds such as MnO_4^-, the olefin reacts directly with a O=Mn=O functionality of MnO_4^- in a [2 + 3] manner to form a metalladioxolane, a five-membered metallacycle[13,14] (structure **2** in Scheme 1). The intermediacy of a metallaoxetane (structure **4**) arising from the [2 + 2] addition pathway as suggested by Sharpless *et al.*[15] for chromyl chloride oxidation of olefin was ruled out, at least for MnO_4^-,

by density functional theory (DFT) calculations[11] and corroborated by experimental kinetic isotope effects studies.[7,16] However, for ethylene addition to $Cl_2(O)ReCH_2$, the activation barrier for the [2 + 2] addition pathway across the Re–C bond of the complex was found by Tia and Adei[17] to be lower than the barrier for the [3 + 2] addition across the O–Re–C and O–Re–Cl bonds of $Cl_2(O)ReCH_2$. Deubel *et al.*[18] found that the activation barrier for the [2 + 2] addition pathway becomes lower than the [3 + 2] addition pathways for ketene addition to $LReO_3$ (L = NPH_3, O^-).

Theoretical calculations focusing on the [3 + 2] and [2 + 2] addition pathways were further explored for the transition metal-oxo complexes of the type $LReO_3$ with ethylene.[19,20] Pietsch *et al.*[19] employed a hybrid density functional theory B3LYP in conjunction with the Hay–Wadt relativistic effective core potential (ECP) for Re (LANL2) and the 6-31G* basis set for other ligands, to compare the [2 + 2] and [2 + 3] addition pathways by focusing only on the thermodynamics for ethylene addition to $LReO_3$ (L = Cp*, Cp, Cl, CH_3, OH, OCH_3, O^-) yielding either the metalladioxolane *via* the [3 + 2] addition pathway or the metallaoxetane *via* the [2 + 2] addition pathway. By employing qualitative molecular orbital diagrams they asserted that the π-donor strength of the ligands L is

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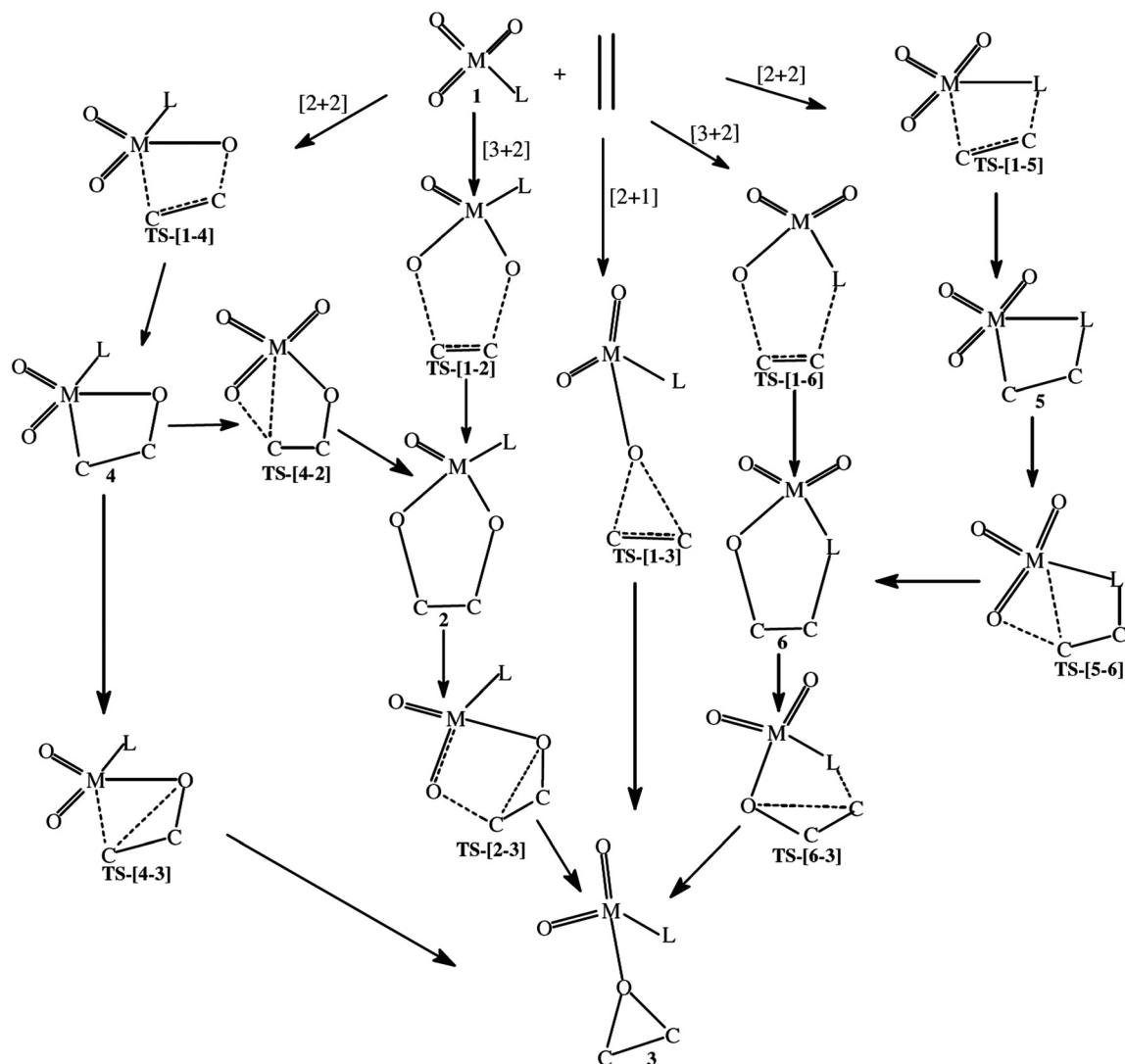
Scheme 1 Proposed concerted pathway for the reaction of LMO$_3$ (M = Re, L = O$^-$, Cl$^-$, CH$_3$O$^-$, CH$_3$, Cp, NPH$_3$) with ethylene.

responsible for the reactivity differences of this type of complex. To verify these claims, Deubel and Frenking[20] reported the calculated potential energy surfaces for the [3 + 2] and [2 + 2] addition of LReO$_3$ (L = O$^-$, Cl, Cp) to ethylene and for the interconversion of the metallaoxetane to the dioxylate, at the B3LYP level[21] in conjunction with relativistic small-core ECPs with a valence basis set splitting (441/2111/21) for Re, and 6-31G(d) all-electron basis sets for all other atoms. Their results indicated that for all complexes of the type LReO$_3$ (L = O$^-$, Cl, Cp), the [2 + 2] pathway has a higher activation barrier than the corresponding [3 + 2] pathway. The activation barriers of the rearrangement of the metallaoxetane intermediate to the dioxylate were calculated to be higher (>50 kcal mol^{-1}). Deubel and Frenking[20] rationalized the reactivity differences using a charge-transfer model and a frontier orbital argument.

Gisdakis and Rösch[22] further extended the works of Pietsch et al.[19] and Deubel and Frenking[20] by assigning charges (q = −1, 0, 1) to the complex LReO$_3{}^q$, such that the systems are isoelectronic to OsO$_4$. They explored the mechanism of the [2 + 3]

cycloaddition of LReO$_3$ (L = O$^-$, CH$_3$, Cl, Cp) to ethylene using the B3LYP functional, with effective core potentials and double-zeta basis sets, LanL2DZ, for the transition metals and 6-311G(d,p) basis sets for H, C, O, and F. Taking a cue from the work of Frenking and Deubel[20] that the [2 + 2] pathway has a higher barrier, Gisdakis and Rösch[22] did not study the formation of the diol from the metallaoxetane along the [2 + 2] addition pathway.

The aim of this work is to extend the works of Pietsch et al.,[19] Deubel and Frenking[20] and Gisdakis and Rösch[22] by employing hybrid density functional theory at the B3LYP/LACVP* level of theory to explore several concerted and stepwise [3 + 2] and [2 + 2] addition pathways for the oxidation of ethylene by LReO$_3$ (L = O$^-$, Cl, Cp, CH$_3$, OCH$_3$, NPH$_3$) and to investigate the possible mechanistic channels for the formation of an epoxide precursor (Schemes 1 and 2). Multiple spin states have been considered in the calculations. This is necessary because organometallic reactions are known to occur on more than the spin surface;[23] many reactions involve
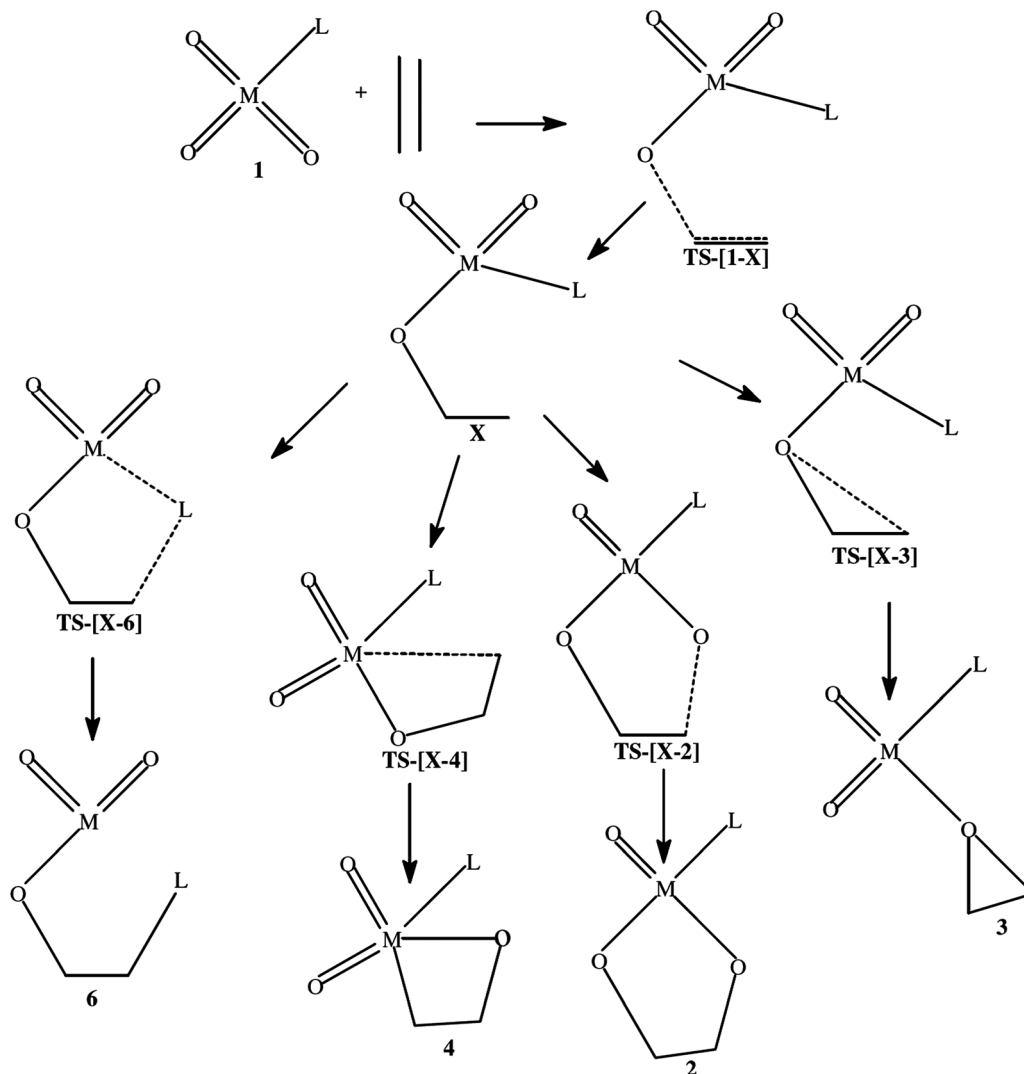
Scheme 2 Proposed stepwise pathway for the reaction of LMO$_3$ (M = Re, L = O$^-$, Cl$^-$ CH$_3$O$^-$, CH$_3$, Cp, NPH$_3$) with ethylene.

several states of different spin.[24] A change of spin state can affect the molecular structure in terms of bond lengths, angular distortions and even overall molecular geometry[25] and spin crossing effects can dramatically affect reaction mechanisms of organometallic transformations.[26]

2. Details of calculation

All calculations were carried out with Spartan'08 V1.2.0 and Spartan'10.1.10 Molecular Modeling programs[27] at the DFT B3LYP/LACVP* level of theory. The B3LYP functional is a Hartree–Fock DFT hybrid functional. 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, for first row elements[28] and the Los Alamos ECP plus double zeta basis set developed by Wadt and Hay for the atoms Na–La, Hf–Bi.[29–31]

The starting geometries of the molecular systems were constructed using Spartan's graphical model builder and minimized interactively using the sybyl force field.[32] All geometries were fully optimized without any symmetry constraints. A normal mode analysis was performed to verify the nature of the stationery 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 – of bonds were fixed at various lengths while the remaining internal co-ordinates 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.

For the ReO$_3$Cl, ReO$_3$(CH$_3$), ReO$_3$(OCH$_3$), ReO$_3$Cp and ReO$_3$(NPH$_3$) systems, the singlet and triplet species were

computed as neutral structures while the doublet and quartet species were computed as anions. For the ReO_4^- system the singlet and triplet species were computed as anions while the doublet and quartet species were computed as neutral structures.

3. Results and discussion

3.1. Reaction of ReO_4^- with ethylene

Fig. 1 shows the relative energies of the main stationary points (reactants, transition states, intermediates and products) involved in the reaction between ReO_4^- and ethylene as well as some of the optimized structures. (The full set of optimized structures for all the systems herein reported is shown in Fig. S1–S6 in the ESI† attached.) The singlet ReO_4^- has all the Re–O bonds equal at 1.738 Å whereas they are different in the doublet and quartet structures. The doublet structure is 72.15 kcal mol^{-1} more stable than the quartet structure; the doublet and quartet species were computed as neutral structures.

On the singlet surface, the [3 + 2] addition of the C=C bond of ethylene across the O=Re=O bonds of ReO_4^- to form dioxorhena-2,5-dioxolane has an activation barrier of 36.3 kcal mol^{-1} and endothermicity of 16.5 kcal mol^{-1} in agreement with the reported activation and reaction energies of 37.7 and 19.4 kcal mol^{-1} by Deubel and Frenking[20] and Gisdakis and Rösch.[22] A triplet dioxorhena-2,5-dioxolane was located and

found to be 25.0 kcal mol^{-1} less stable than the singlet product but a triplet transition state could not be located. The formation of the rhenaoxetane intermediate on a singlet PES by [2 + 2] addition of the C=C bond of ethylene across the Re=O bond of the perrhenate complex has an activation barrier of 46.7 kcal mol^{-1} and an endothermicity of 20.3 kcal mol^{-1}. This also agrees with the work of Deubel and Frenking[20] who calculated a barrier and endothermicity of 47.2 and 21.6 kcal mol^{-1} respectively along the [2 + 2] addition route. A triplet rhenaoxetane has been found to be 48.7 kcal mol^{-1} less stable than the singlet rhenaoxetane. No [3 + 2] or [2 + 2] reaction paths were found on the doublet and quartet surfaces.

The reaction surface was explored for the re-arrangement of the metallaoxetane intermediate to the dioxylate (TS-[4-2] in Scheme 1) as suggested by Sharpless et al.[15] for the chromyl chloride oxidation of olefins. The re-arrangement of the singlet rhenaoxetane to the dioxylate through the transition state has an activation barrier of 16.1 kcal mol^{-1}. No doublet, triplet and quartet transition states were located for the re-arrangement from the rhenaoxetane to the dioxylate. The overall activation barrier for the re-arrangement of the singlet rhenaoxetane to the dioxylate is 16.1 kcal mol^{-1}, which is lower than the activation barrier for the direct [3 + 2] addition of ethylene across the two oxygen atoms of singlet ReO_4^-. However, since the first-step of the reaction, which is the formation of the rhenaoxetane, has a higher activation barrier (46.7 kcal mol^{-1} in Fig. 1), the formation of the dioxylate through this route is unfavorable.
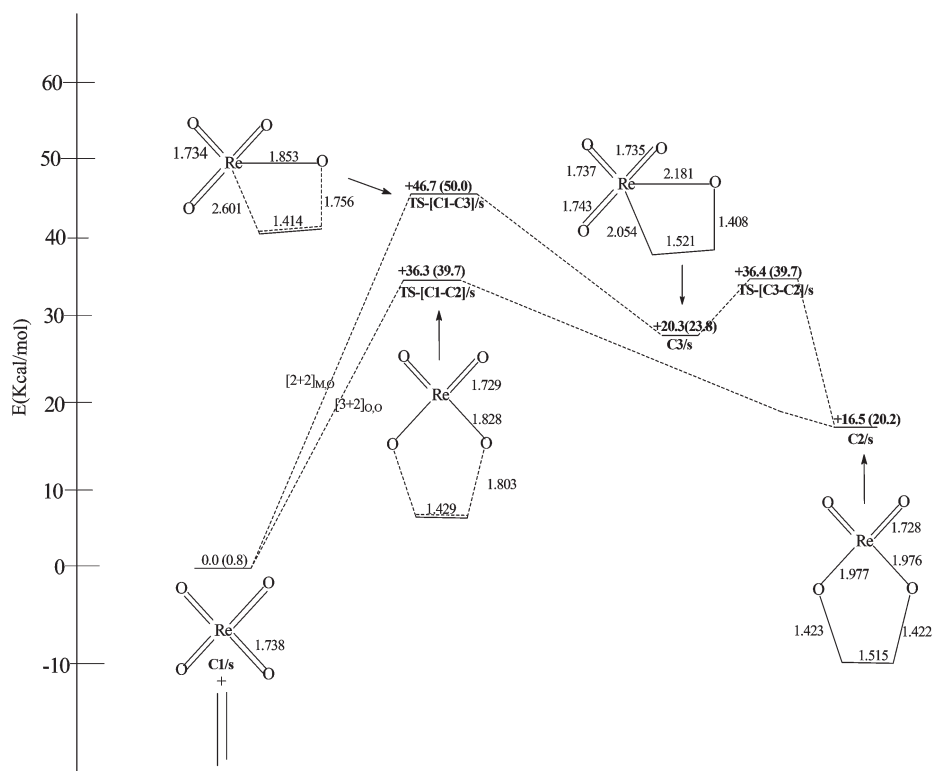

Fig. 1 Energetics of the reactions of ReO_4^- with ethylene. Energies with zero point corrections in parenthesis.

The potential energy surface of the reaction of rhenium tetraoxide with ethylene was further explored in an attempt to locate an epoxide precursor (O_3–Re–OC_2H_4) (**3** in Scheme 1) but no such minimum was found on the reaction surface. Attempts to locate transition states **TS-[4-3]**, **TS-[2-3]** and **TS-[1-3]** of Scheme 1, which could provide a pathway to the formation of the epoxide precursor through re-arrangement of the metallaoxetane, the dioxylate or by direct addition,[33,34] proved futile. All these are indications that the reaction of rhenium tetraoxide with ethylene does not lead to the formation of an epoxide.

3.2. Reaction of ReO₃Cl with ethylene

Fig. 2 and 3 show the relative energies of the main stationary points involved in the reaction between ReO_3Cl and ethylene and some of the optimized structures on the singlet and doublet PESs respectively. The singlet species is 53.7 kcal mol^{-1} more stable than the triplet while the doublet species is 58.9 kcal mol^{-1} more stable than the quartet.

On the singlet surface, the direct [3 + 2] addition of the C=C bond of ethylene across the O=Re=O bonds of ReO_3Cl to form the dioxylate has an activation barrier of 21.0 kcal mol^{-1} and an endothermicity of 0.5 kcal mol^{-1}, which are similar to the energetics obtained in the works of Deubel and Frenking,[20] Gisdakis and Rösch[22] and Boehme *et al.*[35] A triplet dioxylate was found to be 56.3 kcal mol^{-1} more stable than the singlet dioxylate but a triplet transition state for its formation could not be located.

On the doublet surface, the [3 + 2] addition of the C=Cπ bond of ethylene across the O=Re=O bonds of ReO_3Cl can either follow the concerted or stepwise addition mechanism (Scheme 2). For ethylene addition to ReO_3Cl through the

concerted addition pathway, the activation barrier is 33.2 kcal mol^{-1}. On the stepwise addition pathway, the C=Cπ bond attaches itself to an oxo-ligand of the doublet reactant ReO_3Cl **C4/d** through the transition state **TS-[C4-X]/d** to form the intermediate **X/d** (structure **X** in Scheme 2). The activation barrier for the first-step is 29.3 kcal mol^{-1}. The intermediate **X/d** can then re-arrange through transition state **2** in Scheme 2 to form the dioxylate species, with an activation barrier and exothermicity of 43.1 and 18.0 kcal mol^{-1}. Thus, the barrier along the stepwise addition pathway is higher than the concerted route. A quartet dioxylate has been computed to be 31.2 kcal mol^{-1} more stable than the doublet dioxylate but there was no transition state for its formation.

The stepwise [3 + 2] addition of the C=C bond of ethylene across the O=Re–Cl bonds of doublet ReO_3Cl, a pathway that was not reported in the earlier studies of Deubel and Frenking[20] and Boehme *et al.*[35] leads to the intermediate **X/d** through the transition state **TS-[C4-X]/d**. The formation of the intermediate has an activation barrier of 29.3 kcal mol^{-1}. The re-arrangement of the intermediate **X/d** to the five-membered metallacycle **C6/d** through transition state **TS-[X-6]/d** in Scheme 2 has an activation barrier of 15.1 kcal mol^{-1}. The resulting five-membered metallacycle is 14.0 kcal mol^{-1} endothermic. The quartet five-membered metallacycle is computed to be 25.5 kcal mol^{-1} more stable than the doublet. However, no transition state was located connecting the reactants to the product on the quartet surface.

On the singlet surface, the concerted [3 + 2] addition of the C=Cπ bond of ethylene across the O=Re–Cl functionality of ReO_3Cl has an activation barrier of 26.3 kcal mol^{-1} and the resulting five-membered species **C6/s** is 20.2 kcal mol^{-1} endothermic. No stepwise pathway was found for [3 + 2]
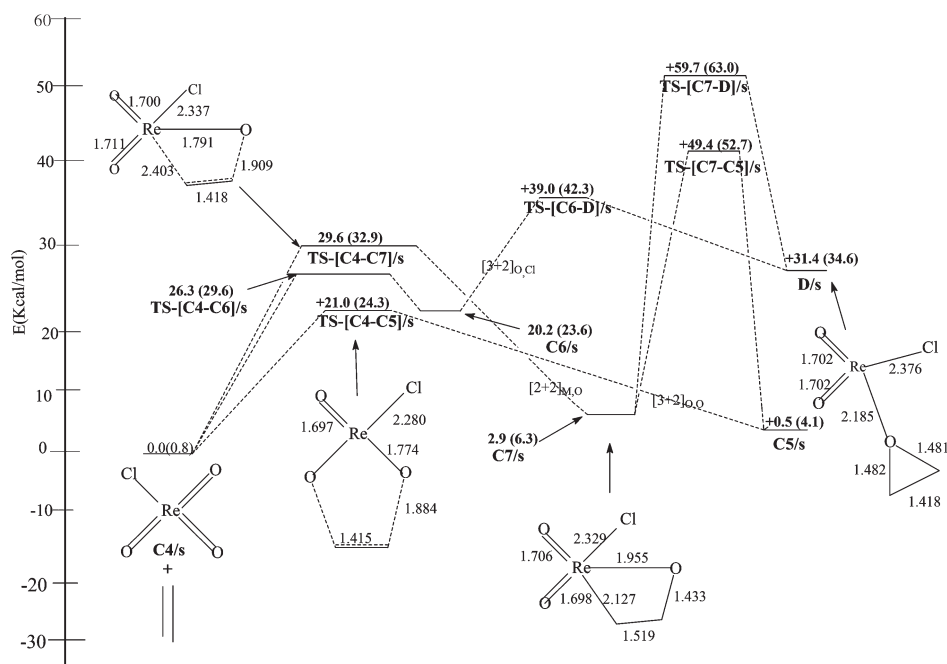

Fig. 2 Energetics of the reactions of ReO₃Cl with ethylene on the singlet PES. Energies with zero point corrections in parenthesis.
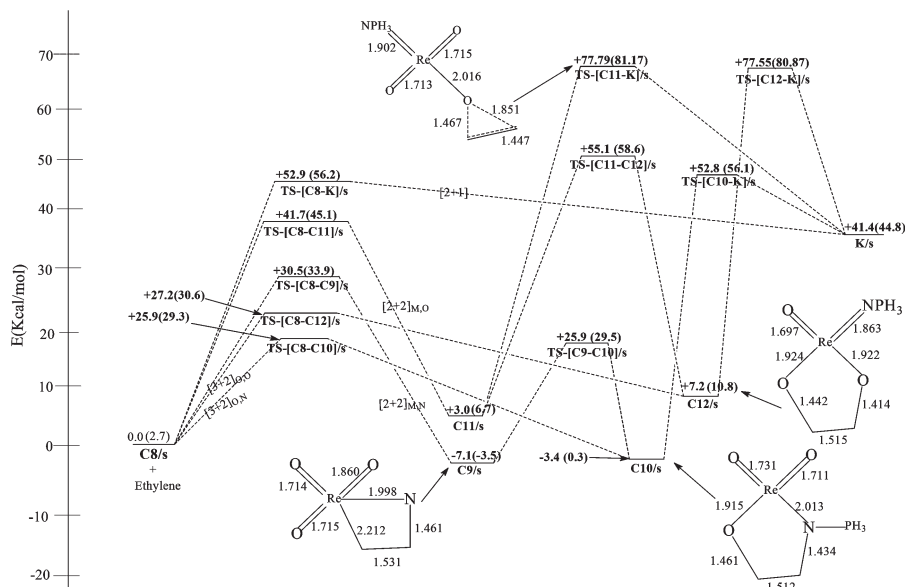
Fig. 3 Energetics of the reactions of ReO₃Cl with ethylene on the doublet PES. Energies with zero point corrections in parenthesis.

addition of the C=Cπ bond of ethylene across the O=Re–Cl functionality of singlet ReO₃Cl on the singlet surface.

The formation of rhenaoxetane on the doublet surface has an activation barrier of 27.3 kcal mol⁻¹ and exothermicity of 7.1 kcal mol⁻¹ while its formation on the singlet surface has an activation barrier of 29.6 kcal mol⁻¹ and endothermicity of 2.9 kcal mol⁻¹. No triplet or quartet transition states could be located. The activation barrier for the re-arrangement of the singlet metallaoxetane to the dioxylate is 46.5 kcal mol⁻¹ while the re-arrangement of the doublet metallaoxetane is to the dioxylate 57.4 kcal mol⁻¹. No triplet and quartet transition state was located for the re-arrangement of the metallaoxetane to the dioxylate. Since the activation barriers for the re-arrangement to form the dioxylate are higher than those for its formation through direct [3 + 2] addition, the formation of the dioxylate through the metallaoxetane is not a competitive route.

The activation energy for the re-arrangement of the singlet five-membered metallacycle **C6/s** to the epoxide precursor is 18.9 kcal mol⁻¹ and the resulting precursor is 11.2 kcal mol⁻¹ less stable than the metallacycle from which it is formed. On the doublet surface, the epoxide precursor could arise from intermediate **X/d** (**X** in Scheme 2) through transition state **TS-[X-D]/d**. The activation barrier and reaction energy along this route are 29.4 and −3.0 kcal mol⁻¹ respectively. On the singlet surface, the rearrangement of the rhenaoxetane to the epoxide precursor has an activation barrier of 56.8 kcal mol⁻¹ and reaction energy of 28.5 kcal mol⁻¹. Also, the activation barrier and reaction energy for the direct one-step [2 + 1] addition of the C=C bond across one oxygen atom of ReO₃Cl

(**TS-[1-3]** in Scheme 1) are 31.2 and 24.7 kcal mol⁻¹ on the doublet surface. Therefore, the most plausible pathway for the formation of the epoxide precursor, if it is to form at all, is by initial [3 + 2] addition across the oxygen and chlorine atoms of singlet ReO₃Cl followed by the re-arrangement to the epoxide precursor on the singlet surface.

3.3. Reaction of ReO₃(NPH₃) with ethylene

The energy profiles of the reactions between ReO₃(NPH₃) and ethylene on the singlet, doublet and triplet PESs are shown in Fig. 4–6 respectively. The singlet reactant is 34.8 kcal mol⁻¹ more stable than the triplet reactant. The formation of the dioxylate on the singlet surface has an activation barrier of 27.2 kcal mol⁻¹ and a reaction energy of 7.2 kcal mol⁻¹ while its formation on the doublet surface has a barrier of 34.4 kcal mol⁻¹ and a reaction energy of 7.7 kcal mol⁻¹.

On the triplet surface, one of the carbon atoms of ethylene attacks an oxo-ligand of ReO₃(NPH₃) to form the intermediate **B/t** (**X** in Scheme 2) through transition state **TS-[C8-B]/t**. The activation barrier and reaction energy for the formation of this intermediate are 21.4 and 4.6 kcal mol⁻¹ respectively. The intermediate then re-arranges to the dioxylate with an activation barrier of 8.2 kcal mol⁻¹ and reaction energy of −15.7 kcal mol⁻¹. A singlet counterpart of the dioxylate has been found to be 45.6 kcal mol⁻¹ less stable than the triplet product.

The [3 + 2] addition of the C=C bond of ethylene across the O=Re=N bonds of ReO₃(NPH₃) on the singlet surface, a pathway which was not explored in the studies of Deubel et al.,[18] has an activation barrier of 25.9 kcal mol⁻¹ and

Fig. 4 Energetics of the reactions of ReO₃(NPH₃) with ethylene on the singlet PES. Energies with zero point corrections in parenthesis.
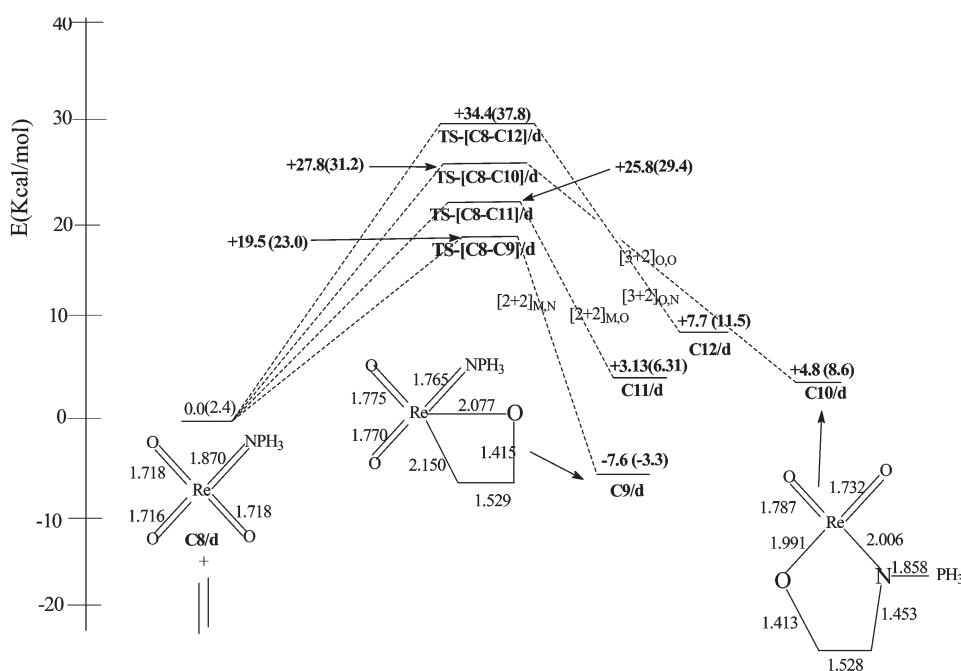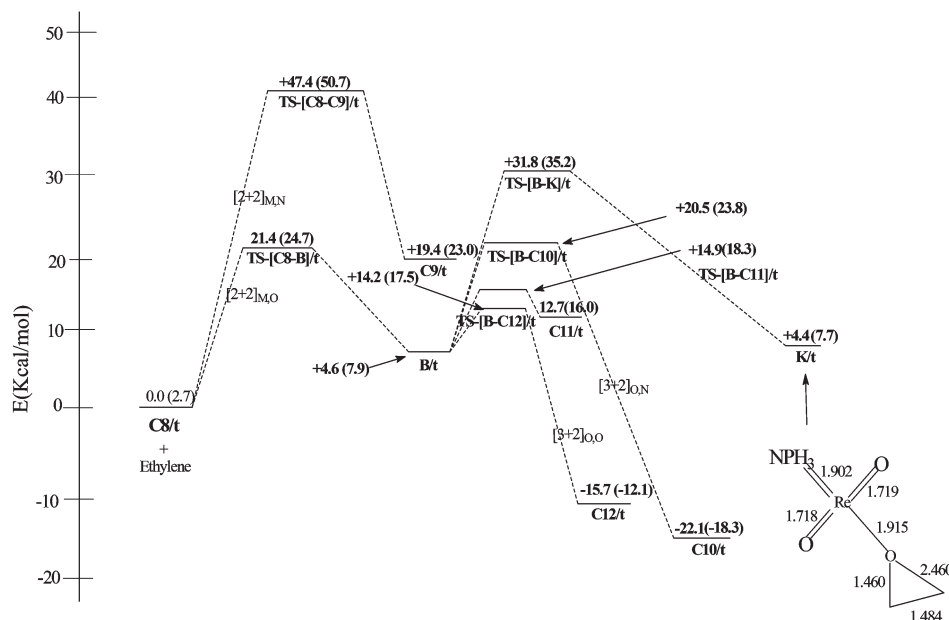

Fig. 5 Energetics of the reactions of ReO₃(NPH₃) with ethylene on the doublet PES. Energies with zero point corrections in parenthesis.

reaction energy of −3.4 kcal mol⁻¹. On the doublet surface, this reaction has an activation barrier of 27.8 kcal mol⁻¹ and reaction energy of 4.8 kcal mol⁻¹.

On the triplet surface, a stepwise addition of one of the C═Cπ of ethylene to an oxo-ligand of ReO₃(NPH₃) leads to an organometallic intermediate **B/t** (**X** in Scheme 2). The activation barrier along this route is 21.4 kcal mol⁻¹. The intermediate then re-arranges to the metallacycle **C10/t**, with an activation barrier of 16.0 kcal mol⁻¹ and reaction energy of −26.6 kcal mol⁻¹.

On the singlet surface, the formation of the rhenaoxetane by [2 + 2] addition has an activation barrier of 41.7 kcal mol⁻¹ and reaction energy of 2.9 kcal mol⁻¹. On the triplet surface, the addition of ethylene across the Re═O bonds of ReO₃(NPH₃) proceeds via a stepwise pathway. The stepwise addition of one of the C═Cπ bonds of ethylene to an oxo-ligand of ReO₃(NPH₃) leads to the formation of the intermediate **B/t**, with an activation barrier of 21.4 and reaction energy of 4.6 kcal mol⁻¹. This intermediate can re-arrange to form the metallaoxetane intermediate, with an

Fig. 6 Energetics of the reactions of ReO$_3$(NPH$_3$) with ethylene on the triplet PES. Energies with zero point corrections in parenthesis.

activation barrier of 10.3 kcal mol^{-1} and reaction energy of 8.2 kcal mol^{-1}.

On the doublet surface the rhenaoxetane formation has a barrier of 25.8 kcal mol^{-1} and a reaction energy of 3.1 kcal mol^{-1}. The quartet rhenaoxetane is 5.7 kcal mol^{-1} more stable than the doublet.

The re-arrangement of the metallaoxetane to the dioxylate on the singlet PES has a barrier of 52.1 kcal mol^{-1} and the reaction energy is 4.2 kcal mol^{-1}. No re-arrangement path was found on the doublet, triplet and quartet surfaces. Thus, since the overall barrier for the re-arrangement of the singlet metallaoxetane (52.1 kcal mol^{-1}) to the dioxylate is higher than the activation barrier for the direct [3 + 2] addition of ethylene to the two oxygen atoms of singlet ReO$_3$(NPH$_3$), the formation of the dioxylate by the re-arrangement of the metallaoxetane to the dioxylate is ruled out.

The [2 + 2] addition of the C=C bond of ethylene across the Re=N bond of ReO$_3$(NPH$_3$) (**TS-[1-5]** in Scheme 1) which was not reported in the work of Deubel *et al.*[20] and Deubel and Frenking[36] has been found to have a barrier and reaction energy of 30.5 and −7.1 kcal mol^{-1} respectively on the singlet surface, 47.4 and 19.4 kcal mol^{-1} respectively on the triplet surface and 19.5 and −7.6 kcal mol^{-1} respectively on the doublet surface. For a related reaction between (O=)$_2$Os-(=NH)$_2$ and ethylene, Deubel and Muniz[37] calculated the activation barrier for the [2 + 2] addition of the Os=N bond across the C=C bond of ethylene to form a four-membered metallacycle to be 36.4 and 34.2 kcal mol^{-1} higher than the [3 + 2] addition across O=Os=NH and O=Os=O moiety to form a five-membered metallacycle. In this work, the activation barrier for the [2 + 2] addition of the Re=N bond of ReO$_3$(NPH$_3$) across the C=C bond of ethylene to form a four-membered metallacycle on the doublet surface is 8.7 and

14.9 kcal mol^{-1} lower than the [3 + 2] addition across O=Re=N and O=Re=O functionality of ReO$_3$(NPH$_3$) to form a five-membered metallacycle. On the singlet surface, the activation barrier for the [2 + 2] addition of the Re=N bond of ReO$_3$(NPH$_3$) across the C=C bond of ethylene is 3.3 and 4.6 kcal mol^{-1} higher than the [3 + 2] addition across O=Os=O and O=Os=NH moiety to form a five-membered metallacycle.

In their study of the reaction of ReO$_3$(NPH$_3$) with ethylene, Deubel *et al.*[18] found the [3 + 2] addition of the C=C bond of ethylene across the O=Re=O bond of singlet ReO$_3$(NPH$_3$) to the dioxylate to be the most favorable reaction. However, in this work the addition across the N–Re=O of the complex ReO$_3$(NPH$_3$), which was not explored in the work of Deubel *et al.* was found to be the most favored pathway.

A search on the reaction surface for the re-arrangement of the singlet, doublet, triplet and quartet four-membered metallacycles **C11** to the five-membered metallacycle **C10** (*i.e.* **TS-[5-6]** in Scheme 1) proved unsuccessful.

The re-arrangement of the singlet five-membered metallacycle **C10** (**TS-[6-3]** in Scheme 1) to the epoxide precursor has an activation barrier of 56.2 kcal mol^{-1} and exothermicity of 44.5 kcal mol^{-1}. On the triplet surface, the epoxide precursor arises from the re-arrangement of the intermediate **B/t**, with an activation barrier of 27.3 kcal mol^{-1} and reaction energy of −0.2 kcal mol^{-1}. The re-arrangement of the singlet five-membered metallacycle **C12/s** to the epoxide precursor has an activation barrier of 70.4 kcal mol^{-1} and endothermicity of +34.0 kcal mol^{-1} while the re-arrangement of the metallaoxetane to the epoxide precursor has an activation barrier of 74.8 kcal mol^{-1} and endothermicity of +38.2 kcal mol^{-1}. Also, the activation barrier and reaction energy for the formation of the epoxide precursor from direct attack of the C=C bond on

the oxygen atom of $ReO_3(NPH_3)$ has been computed to be 52.9 and 41.1 kcal mol^{-1} respectively. Therefore, the most plausible pathway for the formation of the epoxide precursor, if it is to form at all, is through the [2 + 2] addition to form intermediate **B/t** (**X** in Scheme 2) followed by re-arrangement to the epoxide precursor.

3.4. Reaction of $ReO_3(CH_3)$ with ethylene

The optimized geometries and the energy profile of the reaction of $ReO_3(CH_3)$ with ethylene is shown in Fig. 7. The singlet reactant is 68.0 kcal mol^{-1} more stable than the triplet while the doublet is 72.5 kcal mol^{-1} more stable than the quartet.

The formation of the dioxylate by [3 + 2] addition of ethylene across the O=Re=O bond of $ReO_3(CH_3)$ has activation barriers and reaction energies of 33.8 and 17.3 kcal mol^{-1} respectively one the singlet surface, which are similar to the activation barrier and reaction energy reported by Gisdakis and Rösch,[22] and 38.1 kcal mol^{-1} and 12.50 kcal mol^{-1} respectively on the doublet surface. The formation of the rhenaoxetane by [2 + 2] addition of the C=C bond of ethylene across the Re=O bond of $ReO_3(CH_3)$ complex has been found to occur on both the singlet and doublet surfaces. The formation of the rhenaoxetane has an activation barrier and reaction energy of 47.6 kcal mol^{-1} and 4.8 kcal mol^{-1} respectively on the singlet surface and 25.9 kcal mol^{-1} and 1.2 kcal mol^{-1} respectively on the doublet surface. Pietsch et al.[19] in a thermodynamic study of the reaction $ReO_3(CH_3)$ with ethylene found the dioxylate and oxetane to be endothermic by 31 and 10 kcal

mol^{-1} respectively. In this work, the dioxylate and metallaoxetane computed on the singlet and doublet PES are endothermic, while dioxylate and metallaoxetane computed on the triplet and quartet reaction surfaces are exothermic.

The re-arrangement of the metallaoxetane to the dioxylate (**TS-[4-2]** in Scheme 1) has an activation barrier of 48.8 kcal mol^{-1} on the singlet surface and 53.7 kcal mol^{-1} on the triplet surface. No re-arrangement paths were located on the doublet and quartet surfaces. Since the lowest activation barrier for the re-arrangement of the singlet metallaoxetane to the dioxylate (48.8 kcal mol^{-1}) is higher than the activation barrier for the direct [3 + 2] addition of the C=Cπ bond of ethylene across O=Re=O bond of singlet $ReO_3(CH_3)$, the formation of the singlet dioxylate will proceed from the direct [3 + 2] addition of ethylene across the two oxygens of singlet $ReO_3(CH_3)$ rather than through the initial [2 + 2] addition route.

The PES for the reaction of $ReO_3(CH_3)$ with ethylene was explored in an attempt to establish a pathway for epoxide precursor formation through re-arrangement of the metallaoxetane, the dioxylate or by direct [2 + 1] addition. The search for a transition state (i.e. **TS-[2-3]** in Scheme 1) for the re-arrangement of the dioxylate to the epoxide precursor was not fruitful, indicating that such a transformation may not occur. The rearrangement of the metallaoxetane to the epoxide precursor has activation barriers and reaction energies of 65.5 kcal mol^{-1} and +38.4 kcal mol^{-1} respectively on the singlet surface and 29.5 kcal mol^{-1} and +24.7 kcal mol^{-1} respectively on the doublet surface. The activation barrier and reaction energy for
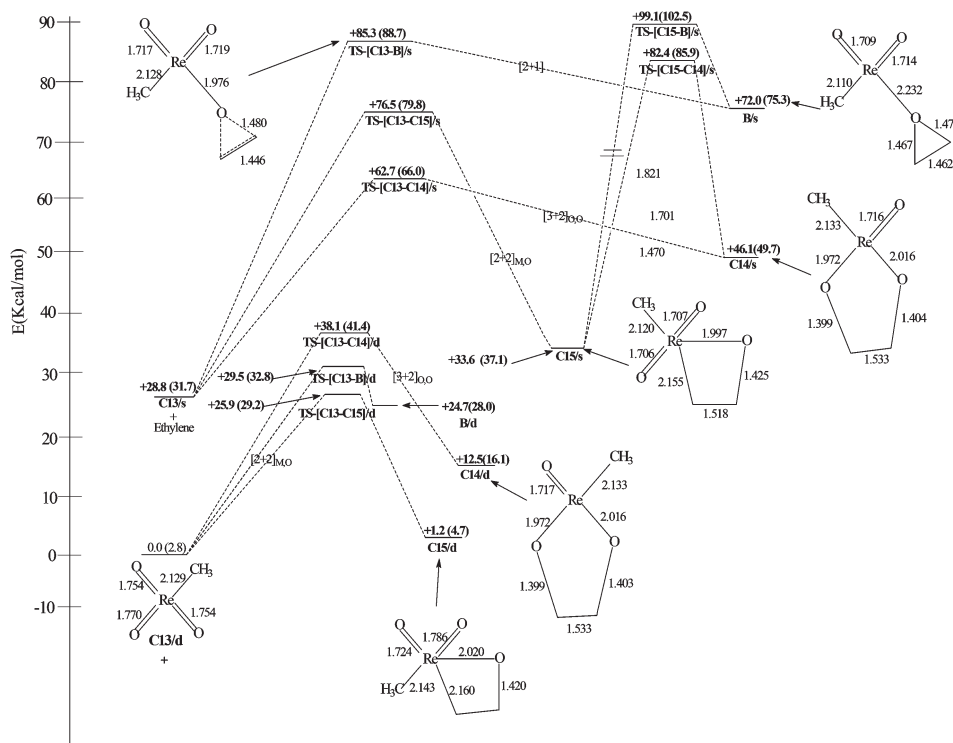

Fig. 7 Energetics of the reactions of $ReO_3(CH_3)$ with ethylene (s = singlet, d = doublet). [a]Energies with zero point corrections in parenthesis. [a]Note that the singlet structures and the doublet structures are not isoelectronic and therefore their energies are not to be compared directly.

the formation of the singlet epoxide precursor from direct attack of the C=C bond on the oxygen atom of ReO$_3$(CH$_3$) has been computed to be 56.5 and +43.1 kcal mol^{-1}. Therefore if reactions considered here are irreversible, then the most plausible pathway for the formation of the epoxide precursor may be direct [2 + 1] addition on the doublet surface.

3.5. Reaction of ReO$_3$(OCH$_3$) with ethylene

Fig. 8 shows the optimized geometries and relative energies of the main stationary points involved in the reaction between ReO$_3$(OCH$_3$) and ethylene. The singlet reactant is 64.1 kcal mol^{-1} more stable than the triplet while the doublet reactant is 60.1 kcal mol^{-1} more stable than the quartet.

The formation of the dioxylate by [3 + 2] addition of the C=C bond of ethylene across the O=Re=O functionality of ReO$_3$(OCH$_3$) has activation barriers and reaction energies of 26.3 kcal mol^{-1} and +3.9 kcal mol^{-1} respectively on the singlet surface and 37.0 kcal mol^{-1} and +5.8 kcal mol^{-1} on the doublet surface. No pathways were found on the triplet and quartet surfaces.

The formation of the rhenaoxetane by [2 + 2] addition of the C=C bond of ethylene across the Re=O bond of ReO$_3$(OCH$_3$) has activation barriers and reaction energies of 30.6 and 6.2 kcal mol^{-1} respectively on the singlet surface and 31.6 kcal mol^{-1} and −2.0 kcal mol^{-1} respectively on the doublet surface. The triplet rhenaoxetane is 35.9 kcal mol^{-1} more stable than the singlet while the quartet is 10.6 kcal mol^{-1} more stable than the doublet. The re-arrangement of

the metallaoxetane to the dioxylate has a barrier of 42.4 kcal mol^{-1} on the singlet surface and 36.2 kcal mol^{-1} on the doublet surface. No triplet or quartet transition states were located for re-arrangement of the metallaoxetane to dioxylate. Since the re-arrangement of the doublet metallaoxetane to the dioxylate has an activation barrier (36.2 kcal mol^{-1}) comparable to that for the initial [3 + 2] addition of C=Cπ of ethylene across O=Re=O of doublet ReO$_3$(OCH$_3$) (37.0 kcal mol^{-1}) and the barrier for the metallaoxetane formation is lower (31.6 kcal mol^{-1}), the formation of the dioxylate could proceed from the two-step process involving formation of the metallaoxetane. However, on the singlet surface the dioxylate will proceed from the direct [3 + 2] addition of ethylene across the two oxygen atoms of singlet ReO$_3$(OCH$_3$) and not from the re-arrangement of the metallaoxetane.

An epoxide precursor was optimized from the reaction of ReO$_3$(OCH$_3$) with ethylene. The rearrangement of the singlet four-membered metallaoxetane to the epoxide precursor has an activation barrier of 61.8 kcal mol^{-1} and reaction energy of 27.8 kcal mol^{-1}. The activation barrier and reaction energy for the formation of the singlet epoxide precursor from direct attack of the C=C bond on the oxygen atom of ReO$_3$(OCH$_3$) has been computed to be 60.4 and +34.0 kcal mol^{-1} respectively while that on the doublet surface is 32.7 kcal mol^{-1} and +26.0 kcal mol^{-1} respectively. Therefore, the most plausible pathway for the formation of the epoxide, if it is to form at all, is by direct [2 + 1] addition on the doublet surface since it has the lowest activation barrier.
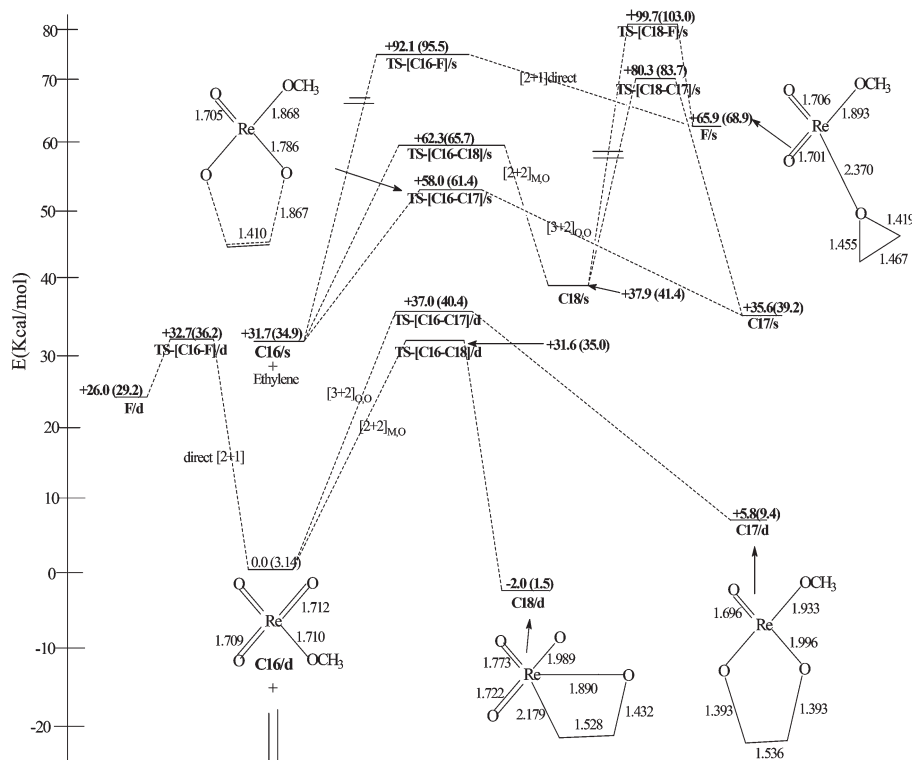

Fig. 8 Energetics of the reactions of ReO$_3$(OCH$_3$) with ethylene (s = singlet, d = doublet). [b]Energies with zero point corrections in parenthesis. [b]Note that the singlet structures and the doublet structures are not isoelectronic and therefore their energies are not to be compared directly.

3.6. Reaction of ReO₃Cp with ethylene

Fig. 9 shows the optimized geometries and relative energies of the main stationary points involved in the reaction between ReO₃Cp and ethylene. In the singlet reactant, the cyclopentadienyl ligand (Cp) is bonded to the metal center in a η^5-fashion *i.e.* Re–C (Cp) = 2.486, 2.511, 2.518, 2.492 and 2.458 Å, in agreement with work of Deubel and Frenking.[20,36] No doublet, triplet and quartet species could be located for the reactant.

On the singlet PES, the [3 + 2] addition of the C=C bond of ethylene across the O=Re=O bonds of ReO₃Cp to form the metalladioxolane intermediate has an activation barrier of 13.60 kcal mol⁻¹ and reaction energy of −18.50 kcal mol⁻¹, which is in agreement with the activation and reaction energies reported by Deubel and Frenking[20] and Gisdakis and Rösch.[22] The Cp ligand in the singlet [3 + 2] transition state structure shows η^5-bonding to the metal centre *i.e.* (Re–C (Cp) = 2.400, 2.453, 2.447, 2.540, 2.557 Å). It also shows a η^5-bonding fashion in the singlet ReO₃Cp dioxylate (Re–C (Cp) = 2.336, 2.329, 2.407, 2.519, 2.472 Å) which disagrees with the η^3-bonding fashion Deubel and Frenking[20] reported for the ReO₃Cp-dioxylate.

On the singlet PES, the formation of the rhenaoxetane by [2 + 2] addition of the C=C bond of ethylene across the Re=O bond of ReO₃Cp complex has an activation barrier of 33.00 kcal mol⁻¹ and reaction energy of −5.76 kcal mol⁻¹. The Cp ligand in the singlet [2 + 2] transition state structure

shows η^3-bonding to the metal centre *i.e.* (Re–C (Cp) = 2.227, 2.744, 2.793 Å) while in the intermediate it shows a η^2-bonding mode to the Re centre, (Re–C (Cp) = 2.174, 2.923 Å). This bonding mode is in disagreement with the work of Deubel and Frenking[20,36] who observed a η^1-bonding for the ReO₃Cp-oxetane intermediate. No metallaoxetane intermediates were located on the doublet, triplet and quartet PES.

In the thermodynamic study of the reaction of ReO₃Cp with ethylene, Pietsch *et al.*[19] asserted that strong π-bonding ligands such as Cp thermodynamically favor dioxylate formation because of π-bond strain relief. Pietsch *et al.*[19] had calculated the dioxylate to be exothermic by 8 kcal mol⁻¹ while the metallaoxetane was endothermic by 5 kcal mol⁻¹. In this work, the dioxylate and the oxetane products are both exothermic, but the dioxylate is more stable.

The re-arrangement of the metallaoxetane to the dioxylate appears to occur exclusively on the singlet PES. The activation barrier for this step is 70.8 kcal mol⁻¹. Since the activation barrier for the direct [3 + 2] addition of C=Cπ of ethylene across the O=Re=O bond of singlet ReO₃Cp (13.6 kcal mol⁻¹) is lower than the barrier for the re-arrangement of the metallaoxetane to the dioxylate, the formation of the dioxylate from the [2 + 2] addition route is ruled out for this system. The potential energy surface of the reaction of rhenium tetraoxide with ethylene was further explored in an attempt to locate an epoxide precursor (CpO₂–Re–OC₂H₄) (**3** in Scheme 1), but no
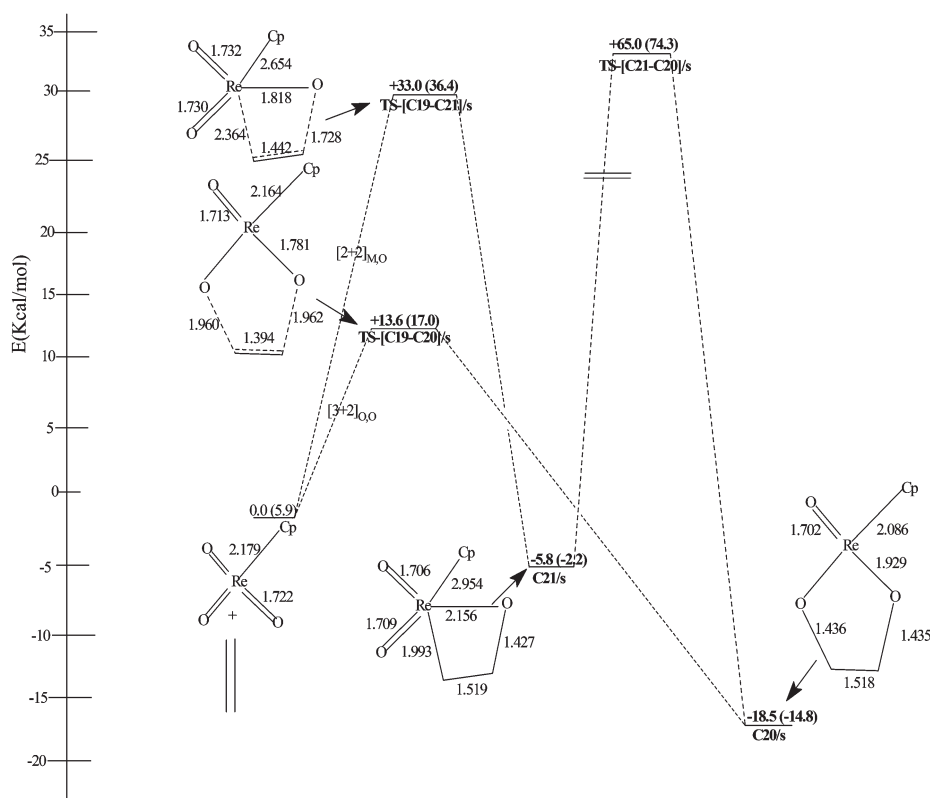

Fig. 9 Energetics of the reactions of ReO₃Cp with ethylene. Energies with zero point corrections in parenthesis.

such minimum was found on these reaction surfaces. This is in agreement with the findings of Burrell *et al*,[38] Herrmann *et al.*,[39] Klahn-Olive *et al.*[40] and Kühn *et al.*[41] who reported that CpReO$_3$ reacts with olefins to predominantly form dioxylates (**2** in Scheme 1).

4. Conclusion

The following conclusions are drawn from the results presented.

1. On the singlet surface, the [3 + 2] addition leading to the formation of a dioxylate intermediate is the predominantly favored pathway in the complexes studied; it is favored over the [2 + 2] addition pathway leading to the formation of a metallaoxetane intermediate for the complexes LReO$_3$ (L = O$^-$, Cl, CH$_3$, OCH$_3$, Cp, NPH$_3$). The activation barriers for the formation of the dioxylate follows the order O$^-$ > CH$_3$ > NPH$_3$ > CH$_3$O$^-$ > Cl$^-$ > Cp and the reaction energies follow the order CH$_3$ > O$^-$ > NPH$_3$ > CH$_3$O$^-$ > Cl$^-$ > Cp. This order in the activation barriers for the ligands is exactly the same as that found for the technetium complexes TcO$_3$ (L = O$^-$, Cl, CH$_3$, OCH$_3$, Cp, NPH$_3$) in Aniagyei *et al.*[42]

2. On the doublet PES, the [2 + 2] addition leading to the formation of the metallaoxetane intermediate is favored over dioxylate formation for the ligands L = CH$_3$, CH$_3$O$^-$, Cl$^-$. The activation barriers for the formation of the metallaoxetane intermediate are found to increase for the ligands in the order CH$_3$ < Cl$^-$ < CH$_3$O$^-$ while the reaction energies follow the order Cl$^-$ < CH$_3$O$^-$ < CH$_3$. The subsequent re-arrangement of the metallaoxetane intermediate to the dioxylate is only feasible in the case of ReO$_3$(OCH$_3$).

3. On the triplet surface, the [2 + 2] addition to form the metallaoxetane is favored over the [3 + 2] addition to form the dioxylate for ReO$_3$(NPH$_3$).

4. Of all the complexes studied, the best dioxylating catalyst is ReO$_3$Cp (singlet surface); the best epoxidation catalyst is ReO$_3$Cl (singlet surface); and the best metallaoxetane formation catalyst is ReO$_3$(NPH$_3$) (triplet surface).

5. The ReO$_4^-$ and ReO$_3$Cp reaction surfaces are much 'cleaner' than the rest of the complexes studied *i.e.* there are no side-reactions competing with the formation of the dioxylate and metallaoxetane intermediates. This trend was also observed for the technetium complexes TcO$_3$ (L = O$^-$, Cl, CH$_3$, OCH$_3$, Cp, NPH$_3$) in Aniagyei *et al.*[42]

6. There does not appear to be a spin-crossover in any of the pathways studied.

Acknowledgements

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