

Ethylene addition to group-6 transition metal oxo complexes – A theoretical study[☆]

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Abstract

Quantum chemical calculations using density functional theory (B3LYP) were carried out to elucidate the reaction pathways for ethylene addition to the chromium and molybdenum complexes $\text{CrO}(\text{CH}_3)_2(\text{CH}_2)$ (**Cr1**) and $\text{MoO}(\text{CH}_3)_2(\text{CH}_2)$ (**Mo1**). The results are compared with previously published results of the analogous tungsten system $\text{WO}(\text{CH}_3)_2(\text{CH}_2)$ (**W1**). The comparison of the group-6 elements shows that the molybdenum and tungsten compounds **Mo1** and **W1** have a similar reactivity while the chromium compound has a more complex reactivity pattern. The kinetically most favorable reaction pathway for ethylene addition to **Mo1** is the $[2+2]_{\text{Mo,C}}$ addition across the $\text{Mo}=\text{CH}_2$ double bond which has an activation barrier of only 8.4 kcal/mol. The reaction is slightly exothermic with $\Delta E_{\text{R}} = -0.6$ kcal/mol. The $[2+2]_{\text{Mo,O}}$ addition across the $\text{Mo}=\text{O}$ double bond and the $[3+2]_{\text{C,O}}$ addition have much higher barriers and are strongly endothermic. The thermodynamically mostly favored reaction is the $[1+2]_{\text{Mo}}$ addition of ethylene to the metal atom which takes place after prior rearrangement of the Mo(VI) compound **Mo1** to the Mo(IV) isomer **Mo1g**. The reaction is -19.2 kcal/mol exothermic but it has a large barrier of 34.5 kcal/mol. The kinetically and thermodynamically most favorable reaction pathway for ethylene addition to the chromium homologue **Cr1** is the multiple-step process with initial rearrangements **Cr1** \rightarrow **Cr1c** \rightarrow **Cr1g** which are followed by a $[1+2]_{\text{Cr}}$ addition yielding an ethylene π complex **Cr1g** + $\text{C}_2\text{H}_4 \rightarrow$ **Cr1g-1**. The highest barrier comes from the first step **Cr1** \rightarrow **Cr1c** which has an activation energy of 14.2 kcal/mol. The overall reaction is exothermic by -26.3 kcal/mol.

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1. Introduction

Numerous quantum chemical studies have shown that the initial step of the addition of olefins to OsO_4 is a concerted $[3+2]$ reaction yielding an osma-2,5-dioxolane as a product [1]. Subsequently, this intermediate eliminates the *cis*-dihydroxylated olefin. This reaction pathway has a significantly lower activation barrier compared to the alternative two-step reaction pathway initiated by a $[2+2]$ cycloaddition of the olefin with OsO_4 followed by a

rearrangement of the resulting osmaoxetane. Further quantum chemical investigations [2] concluded that other metal oxides like RuO_4 and ReO_3^- also prefer a $[3+2]$ cycloaddition pathway rather than a $[2+2]$ one [3]. The presence of an imido group does not change the reactivity significantly. Deubel and Muñoz found that for $\text{Os}(\text{NH}_2)_2\text{O}_2$ the $[3+2]$ cycloaddition pathway is still preferred over the $[2+2]$ one [4]. A decrease of activation energies was predicted by the authors in the order $\text{O/O} > \text{O/NH} > \text{NH/NH}$.

Recently, we reported that the reactivity changes when a carbon–metal double bond is present. For the ethylene addition to $\text{OsO}_3(\text{CH}_2)$ and $\text{OsO}_2(\text{CH}_2)_2$, the $[2+2]$ cycloaddition across the transition metal–carbon double bond becomes competitive [6,7] and for $\text{ReO}_2(\text{CH}_3)(\text{CH}_2)$ and $\text{WO}(\text{CH}_3)_2(\text{CH}_2)$, it becomes even more favorable [7,8] than the $[3+2]$ reaction pathway. We extended our

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theoretical investigations of the ethylene addition to the group-6 elements of the periodic table from tungsten to the lighter homologues molybdenum and chromium. In this paper, we present our quantum chemical results of the reaction pathways for the ethylene addition to $\text{MoO}(\text{CH}_3)_2(\text{CH}_2)$ (**Mo1**) and $\text{CrO}(\text{CH}_3)_2(\text{CH}_2)$ (**Cr1**) and compare them with each other and with the recently published data on the tungsten analogue $\text{WO}(\text{CH}_3)_2(\text{CH}_2)$ (**W1**) [8]. The investigations are restricted to molecules in the singlet electronic state. We cannot exclude that higher spin states may play a role in the reactions, but the present work gives an overview of the possible reaction pathways of molybdenum and chromium compounds in the singlet state.

2. Methods

All geometry optimizations were carried out using gradient corrected density functional theory (DFT) employing the B3LYP hybrid functional [9] as implemented [10] in the GAUSSIAN 03 program [11] without any symmetry constraints. Ahlrich's triple zeta basis set (TZVP) [12] was used for the elements O, C and H. For the transition metals, the Stuttgart/Köln relativistic effective core pseudo potentials (ECP) replacing 28 (for molybdenum) respectively 10 (for chromium) core electrons was employed in combination with a (311111/22111/411) (for molybdenum) [13] respectively, (311111/22111/411/1) (for chromium) [14] valence basis set. This combination is denoted as basis set I. Analytical vibrational harmonic frequencies were calculated at all stationary points to verify their nature (minimum, transition state or higher order saddlepoint). Intrinsic reaction coordinate (IRC) [15] calculations were carried out to ensure the connectivity of the minima and transition states. For transition states with an imaginary mode of too small magnitude, dynamic reaction path (DRP) [16] calculations were done instead. The DRP calculations were carried out

using the frog module of the TURBOMOLE program [17]. Here, a slightly different valence basis set for the transition metals was employed. For molybdenum, a (31111/411/311) valence basis set was used in conjunction with the Stuttgart/Köln ECPs whereas for chromium, no ECP was employed. Instead Ahlrich's all-electron triple zeta basis set (842111/6311/411) [18] was used. Additional B3LYP single point energies were computed at all transition states and minima with a larger basis set denoted as basis set II. There, the correlation consistent triple zeta basis sets of Dunning (cc-pVTZ) [19] were used for the elements O, C and H. The transition metal basis set is augmented by two sets of *f* and one set of *g* functions derived by Martin and Sundermann [20]. All energies discussed in this study relate to B3LYP/II//B3LYP/I and are corrected by the unscaled zero point energy (ZPE) contributions obtained at B3LYP/I unless otherwise stated.

3. Results and discussion

Since the focus of this work lies on the calculated reaction profiles for the addition of ethylene to the molybdenum and chromium compounds, we discuss mainly reaction energies but not the geometries of the calculated species. The full set of coordinates and energies of all compounds is given as [supplementary material](#).

Our previous studies have shown that the transition metal compounds $\text{L}_n\text{M}(=\text{O})(=\text{CH}_2)$ which possess oxo and alkylidene moieties may rearrange to isomers which can be lower in energy than the parent system [5–8]. Therefore, we calculated isomeric forms of **Mo1** and **Cr1** and the transition structures connecting them with the parent system. Fig. 1 shows the reaction profile for the isomerizations of **Mo1**. The optimized equilibrium structures and transition states of the molybdenum species with the most important bond lengths are shown in Fig. 2.

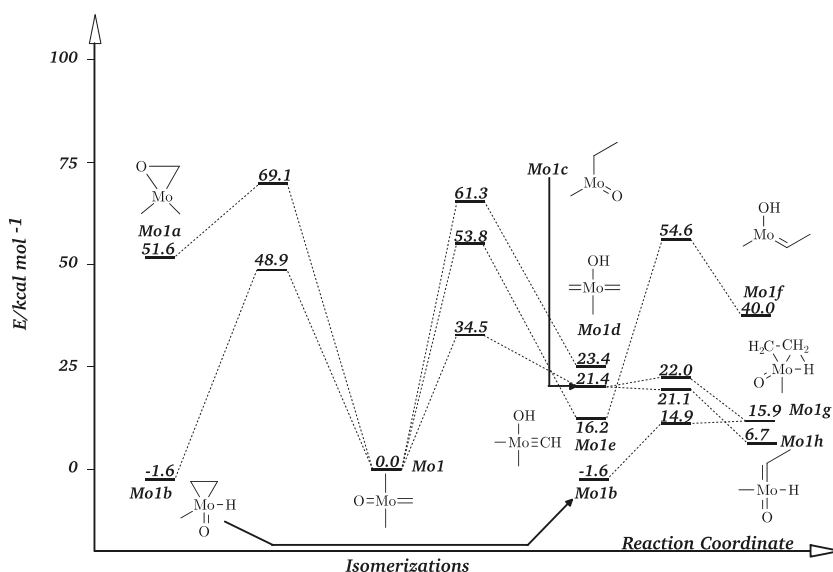


Fig. 1. Calculated reaction profile for the isomerizations of $(\text{O}=\text{Mo})(\text{CH}_3)_2(\text{=CH}_2)$ (**Mo1**) at B3LYP/II//B3LYP/I + ZPE.

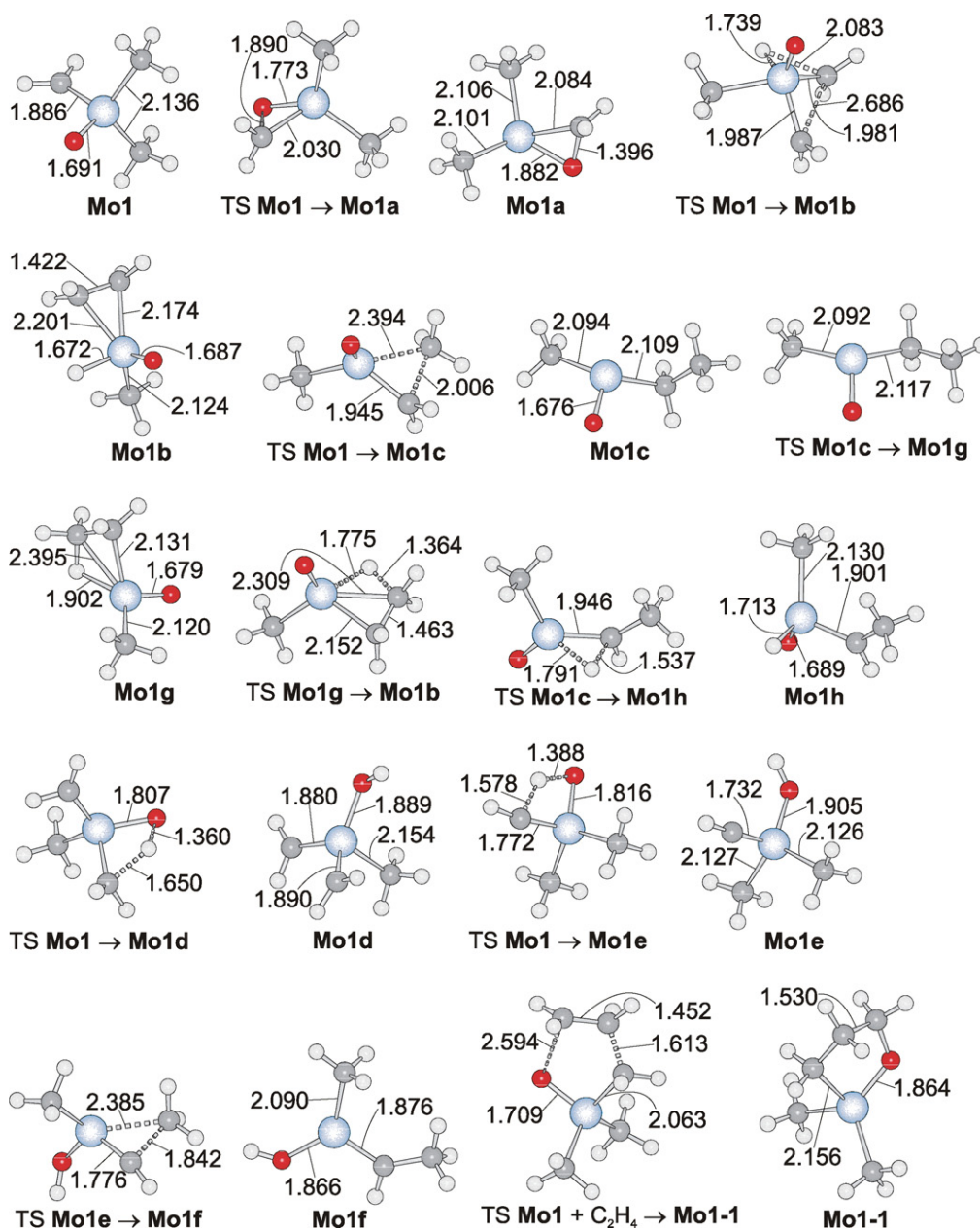


Fig. 2. Optimized molybdenum and tungsten structures with selected atomic distances given in Å.

Eight isomeric forms of **Mo1** were found as minima on the potential energy surface (PES) besides the parent compound. Five species have an acyclic structure (**Mo1c–Mo1f** and **Mo1h**), two isomers have a cyclic geometry (**Mo1a** and **Mo1b**) and one structure is a hydrogen-bridged isomer (**Mo1g**). The cyclic isomers and the associated activation barriers are shown on the left-hand side of Fig. 1, whereas the acyclic and bridged isomers are displayed on the right side. Note that only five isomers are directly accessible via rearrangement of the reference compound **Mo1** (**Mo1a–Mo1e**) while **Mo1f–Mo1h** are formed via multiple-step rearrangements. The cyclic species **Mo1b** is the only isomer which is slightly lower in energy than the parent compound **Mo1**, but the isomerization is exothermic by

only 1.6 kcal/mol and the barrier is very large with 48.9 kcal/mol. The calculations indicate that all five activation energies for rearrangement of **Mo1** yielding the isomers **Mo1a–Mo1e** are quite large. The lowest activation barrier is calculated for **Mo1** → **Mo1c** (34.5 kcal/mol) which is an endothermic reaction. The theoretical data suggest that **Mo1** lies in a rather deep potential well whereas some isomers have a very shallow well because the barriers for further rearrangement are very small. This holds for the processes **Mo1c** → **Mo1g**, **Mo1c** → **Mo1h** and **Mo1g** → **Mo1b**. The energies of the transition states for the latter two reactions are even lower than the energies of the starting molecules after ZPE corrections are made. The isomers **Mo1c** and **Mo1g** are unlikely to be observable species.

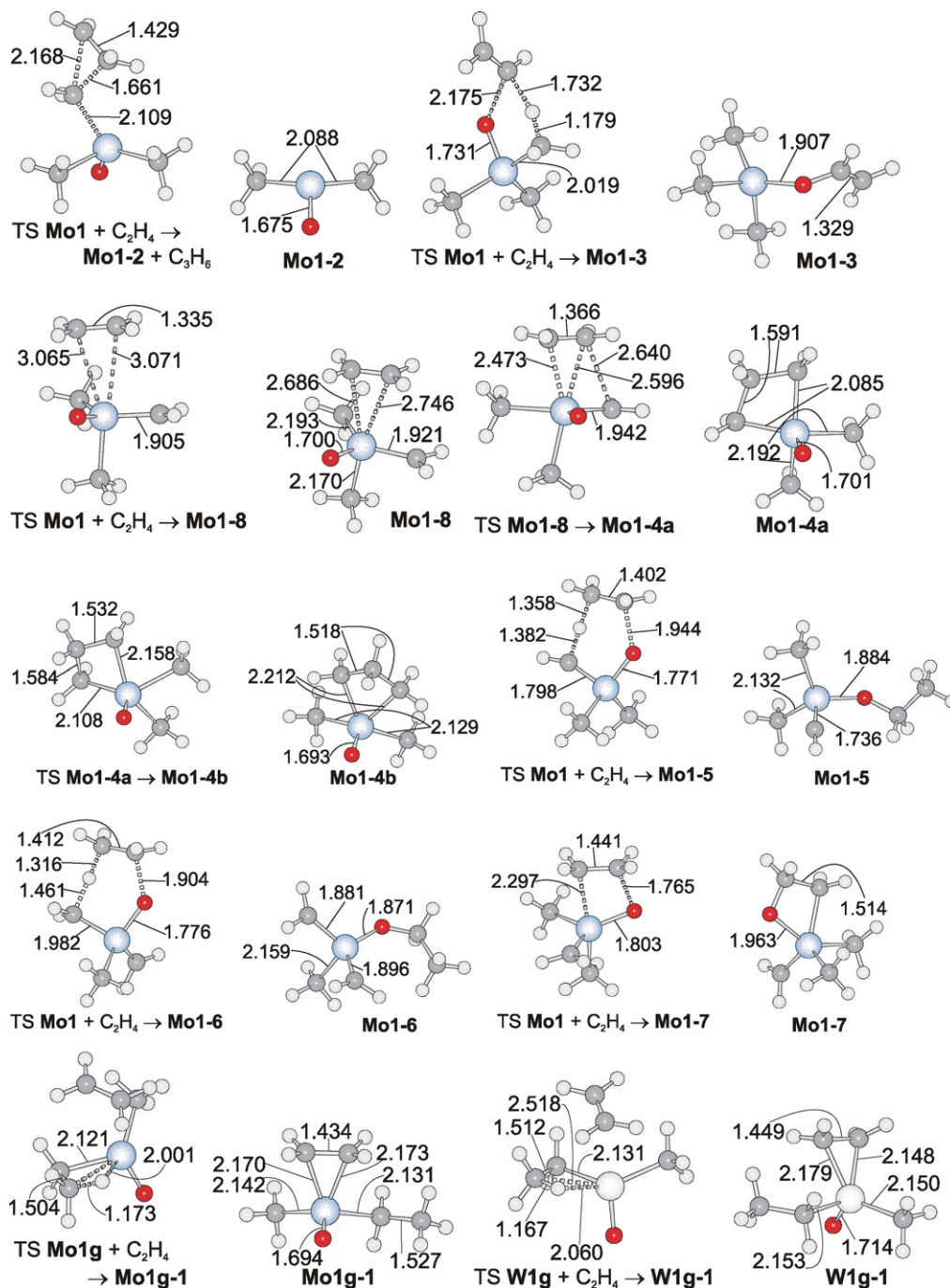


Fig. 2 (continued)

Since the calculated barriers for rearrangement of the parent compound **Mo1** are rather high, we only discuss the addition of ethylene to **Mo1** but not to the other isomers. Fig. 3 shows the theoretically predicted reaction profiles. For the geometries of the energy minima and transition states, see Fig. 2.

Several reaction pathways for concerted [3+2], [2+2] and [1+2] cycloadditions have been found for the reaction **Mo1** + C₂H₄. Fig. 3 shows at the right-hand side the reaction profile for the [2+2] addition of ethylene across the Mo=C bond **Mo1** + C₂H₄ → **Mo1-4a/b** via the precoordi-

nated complex **Mo1-8** which is, however, only a very shallow energy minimum. The species **Mo1-8** further reacts without activation energy if ZPE corrections are considered to the metallacyclobutane **Mo1-4a** which rearranges with a small barrier of 3.1 kcal/mol to the slightly more stable isomer **Mo1-4b**. The overall reaction **Mo1** + C₂H₄ → **Mo1-4b** is kinetically the most favorable reaction pathway for the addition of ethylene to **Mo1**. It is also the only reaction which is exothermic, although the calculated exothermicity of −3.2 kcal/mol is not very large. The [2+2] addition of ethylene across the Mo=O bond yielding the

metallaioxetane **Mo1-7** is the kinetically next favorable reaction which has, however, a clearly higher barrier of 32.9 kcal/mol. The reaction $\text{Mo1} + \text{C}_2\text{H}_4 \rightarrow \text{Mo1-7}$ is endothermic by 28.0 kcal/mol (Fig. 3). The [3+2] addition $\text{Mo1} + \text{C}_2\text{H}_4 \rightarrow \text{Mo1-1}$ and the formal [1+2] addition $\text{Mo1} + \text{C}_2\text{H}_4 \rightarrow \text{Mo1-2} + \text{cyclopropane}$ are slightly less endothermic than the previous reaction but the activation barriers of 44.2 and 45.5 kcal/mol are much higher. The calculations indicate that the addition of ethylene to **Mo1** is another example where a [2+2] addition is kinetically and thermodynamically more favorable than a [3+2] addition.

Fig. 3 shows on the left-hand side three reaction courses where a hydrogen migration takes place during the addition

of ethylene to **Mo1**. All reactions are endothermic and have rather high activation barriers. In the reactions $\text{Mo1} + \text{C}_2\text{H}_4 \rightarrow \text{Mo1-6}$ and $\text{Mo1} + \text{C}_2\text{H}_4 \rightarrow \text{Mo1-5}$ one hydrogen atom migrates from **Mo1** to C_2H_4 while in the reaction $\text{Mo1} + \text{C}_2\text{H}_4 \rightarrow \text{Mo1-3}$ one hydrogen atom moves in the reverse direction. None of the reactions should compete with the [2+2] reaction $\text{Mo1} + \text{C}_2\text{H}_4 \rightarrow \text{Mo1-4a/b}$ which is clearly the kinetically most favorable pathway. The thermodynamically most favorable ethylene addition which is not shown in the reaction profiles is the [1+2]_{Mo} addition of ethylene to the metal atom yielding **Molg-1** (Fig. 2) which takes place after prior rearrangement $\text{Mo1} \rightarrow \text{Molg}$. The reaction is -19.2 kcal/mol exothermic but it has a large barrier of 34.5 kcal/mol.

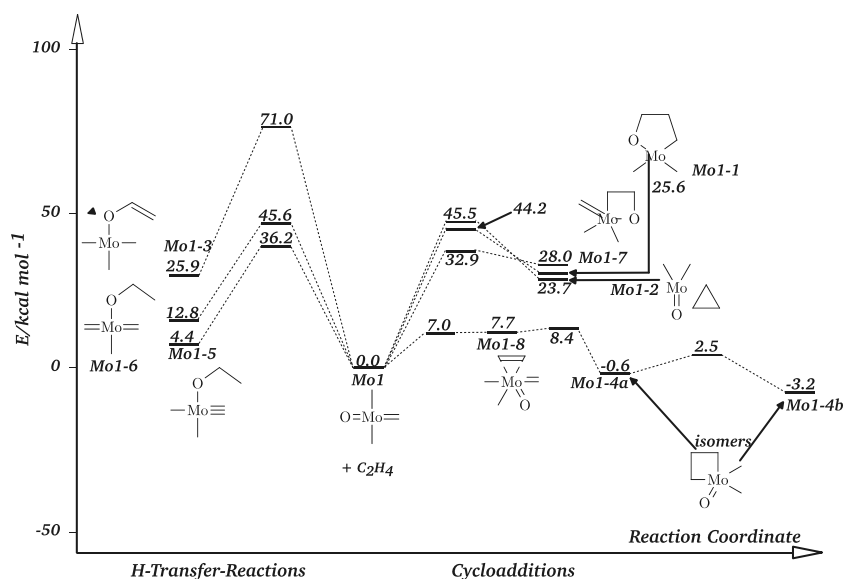


Fig. 3. Calculated reaction profile for the addition of ethylene to $(\text{O}=\text{Mo})(\text{CH}_3)_2(\text{=CH}_2)$ (**Mo1** + C_2H_4) at B3LYP/II//B3LYP/I + ZPE.

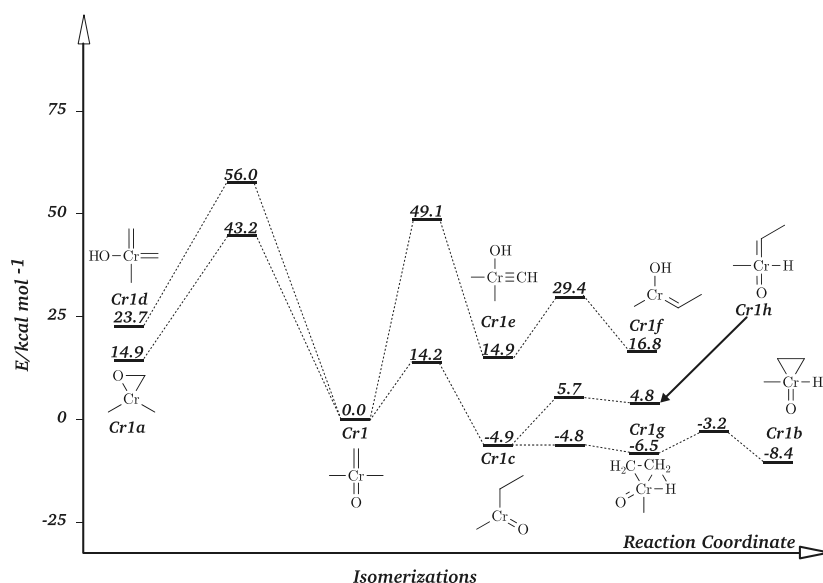


Fig. 4. Calculated reaction profile for the isomerizations of $(\text{O}=\text{Cr})(\text{CH}_3)_2(\text{=CH}_2)$ (**Cr1**) at B3LYP/II//B3LYP/I + ZPE.

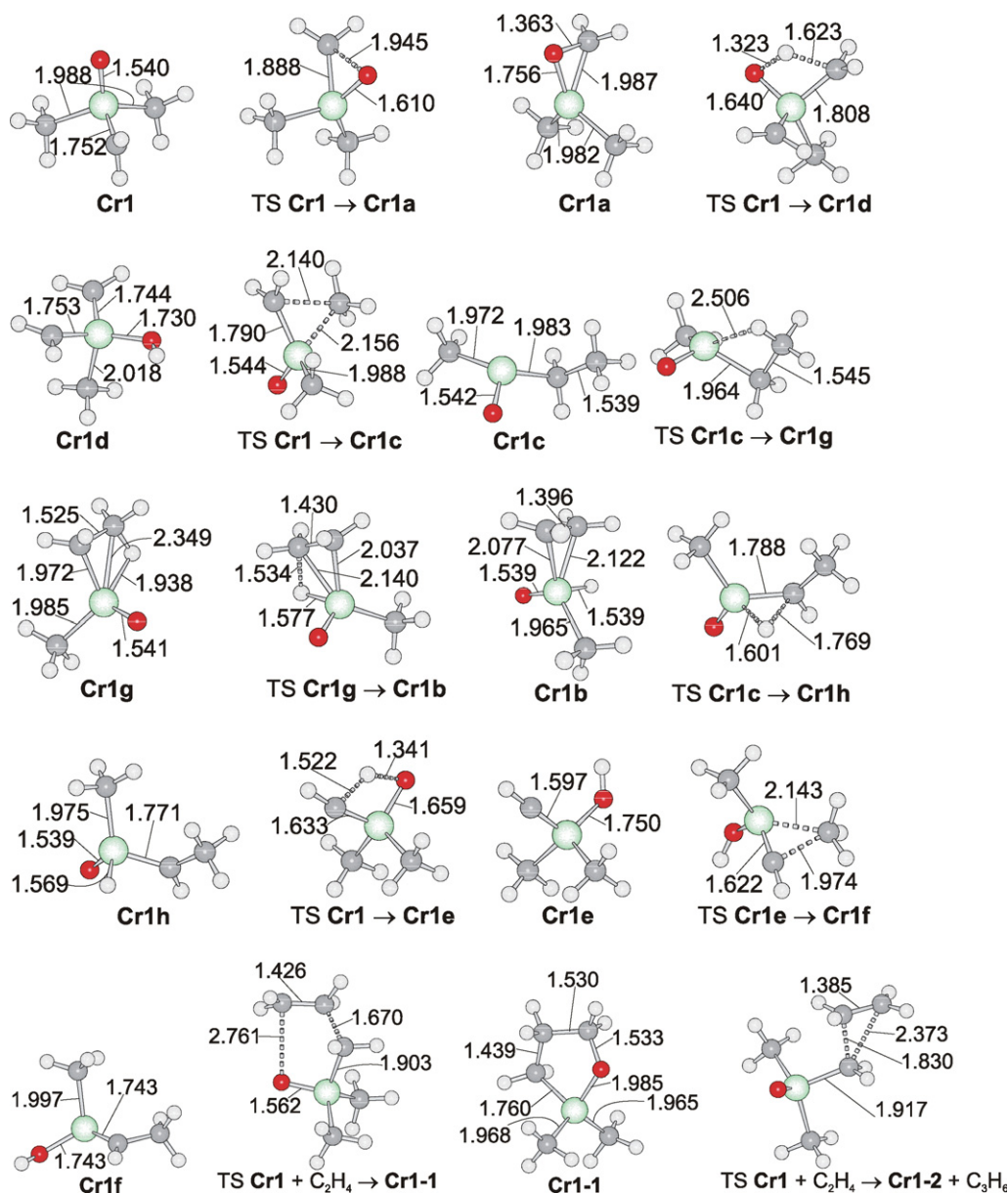


Fig. 5. Optimized chromium structures with selected atomic distances given in Å.

Next we discuss the results for the chromium system $\text{Cr1} + \text{C}_2\text{H}_4$ which exhibits a much higher complexity than the molybdenum compound. Fig. 4 shows the reaction profile for the isomerization reactions of **Cr1**. The optimized equilibrium structures and transition states of the chromium species with the most important bond lengths are shown in Fig. 5.

Unlike the molybdenum homologue **Mo1**, the chromium compound **Cr1** may rearrange with a rather low activation barrier of 14.2 kcal/mol to the energetically lower lying isomer **Cr1c** which is a shallow energy minimum on the PES. The calculations gave three isomers which are close in energy as minima on the PES which rearrange with low activation barriers following the sequence $\text{Cr1c} \rightarrow \text{Cr1g} \rightarrow \text{Cr1b}$. It is interesting to note that the chromium(IV) isomer **Cr1c** is energetically nearly degener-

ate with the chromium(VI) isomer **Cr1b** (Fig. 4) while the molybdenum homologue **Mo1c** is much higher lying than **Mo1b** (Fig. 1). The same holds true for **M1e** and **M1f**. **Cr1c** may also rearrange to the energetically higher lying form **Cr1h** which is, separated by a small barrier from **Cr1c**. Finally, there are three isomerization pathways $\text{Cr1} \rightarrow \text{Cr1a}$, $\text{Cr1} \rightarrow \text{Cr1d}$ and $\text{Cr1} \rightarrow \text{Cr1e}$ which have high activation barriers yielding less stable isomers than the parent molecule.

Because three isomers **Cr1c**, **Cr1g** and **Cr1b** are theoretically predicted to be slightly lower in energy than the parent compound **Cr1** which are kinetically accessible and may therefore play a role in the addition reaction of an olefin, we calculated the reaction profiles for the addition of ethylene to **Cr1**, **Cr1c**, **Cr1g** and **Cr1b**. Fig. 6 shows the results for the reaction $\text{Cr1} + \text{C}_2\text{H}_4$.

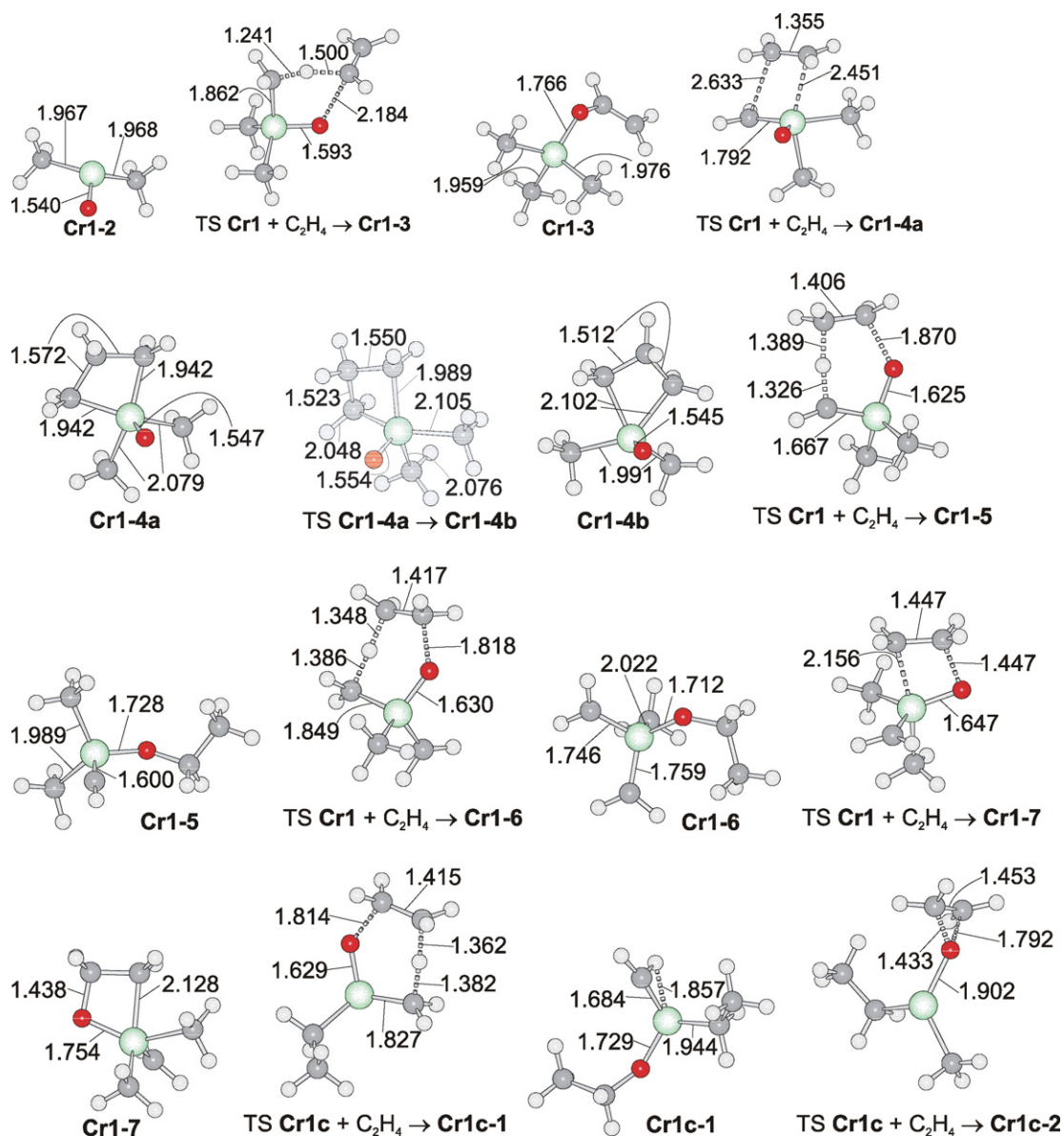


Fig. 5 (continued)

The results for the chromium system which are schematically displayed in Fig. 6 exhibit a similar reaction profile as for the reaction $\text{Mo1} + \text{C}_2\text{H}_4$ (Fig. 3). There are two [2+2] cycloadditions of ethylene across the $\text{Cr}=\text{CH}_2$ and $\text{Cr}=\text{O}$ double bonds yielding the metallacyclobutane **Cr1-4** which has two isomeric forms **Cr1-4a** and **Cr1-4b** and the metallaioxetane **Cr1-7**, respectively. The latter reaction is thermodynamically the least favorable cycloaddition while the reaction $\text{Cr1} + \text{C}_2\text{H}_4 \rightarrow \text{Cr1-4a} \rightarrow \text{Cr1-4b}$ has the lowest activation barrier (14.7 kcal/mol) of all addition reactions which were considered. The latter reaction is nearly thermoneutral. The calculated results for the [3+2] cycloaddition $\text{Cr1} + \text{C}_2\text{H}_4 \rightarrow \text{Cr1-1}$ are very interesting. The theoretical data suggest that the latter reaction is more exothermic but has a much higher activation barrier than the [2+2] cycloaddition $\text{Cr1} + \text{C}_2\text{H}_4 \rightarrow \text{Cr1-4a/b}$. Such a

scenario was originally suggested by Sharpless for the olefin addition to OsO_4 in order to explain the enantioselectivity which is observed when the reaction is carried out in the presence of chinchina alkaloids [22]. The calculations did not support [1] the hypothesis of Sharpless but the present calculations show that other metallaioxetanes may indeed behave as it was wrongly suggested for OsO_4 .

Fig. 6 shows that the formal [1+2] addition $\text{Cr1} + \text{C}_2\text{H}_4 \rightarrow \text{Cr1-2} + \text{cyclopropane}$ is slightly less exothermic than the [3+2] addition $\text{Cr1} + \text{C}_2\text{H}_4 \rightarrow \text{Cr1-1}$ but the activation barrier of 23.7 kcal/mol is lower than that of the latter process. The calculations for the chromium system (Fig. 6) gave the same addition reactions which take place with concomitant hydrogen migration which were found for the molybdenum system (Fig. 3). The reactions $\text{Cr1} + \text{C}_2\text{H}_4 \rightarrow \text{Cr1-3}$, $\text{Cr1} + \text{C}_2\text{H}_4 \rightarrow \text{Cr1-5}$

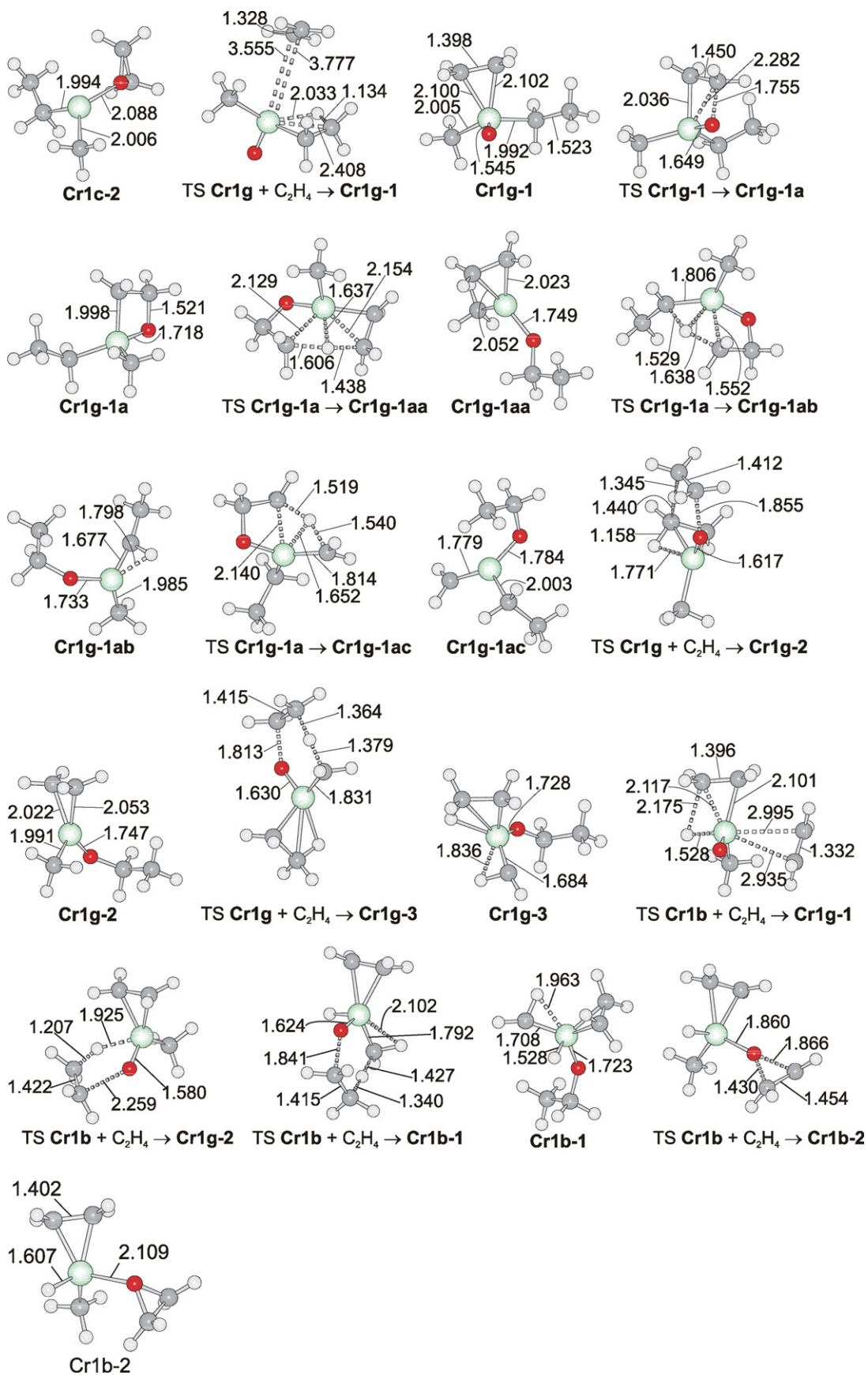


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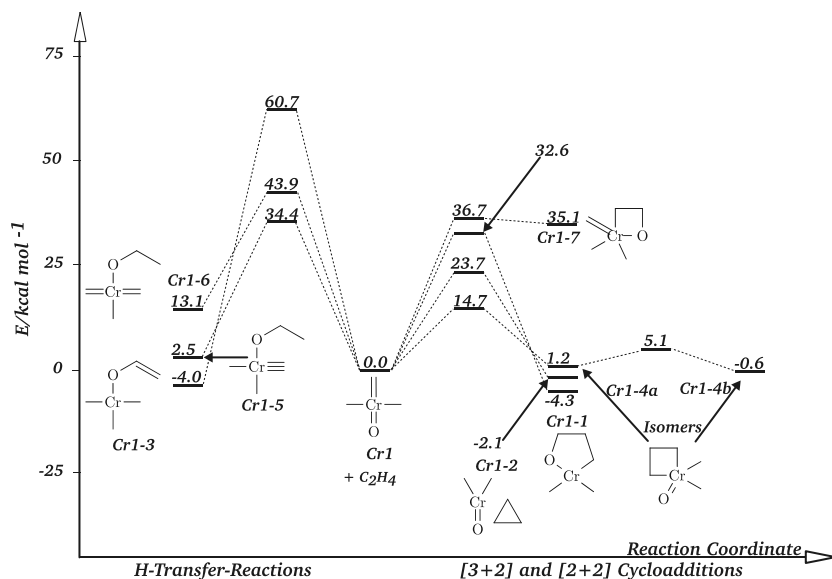


Fig. 6. Calculated reaction profile for the addition of ethylene to $(\text{O}=\text{Cr}(\text{CH}_3)_2(\text{=CH}_2))$ ($\text{Cr1} + \text{C}_2\text{H}_4$) at B3LYP/II//B3LYP/I + ZPE.

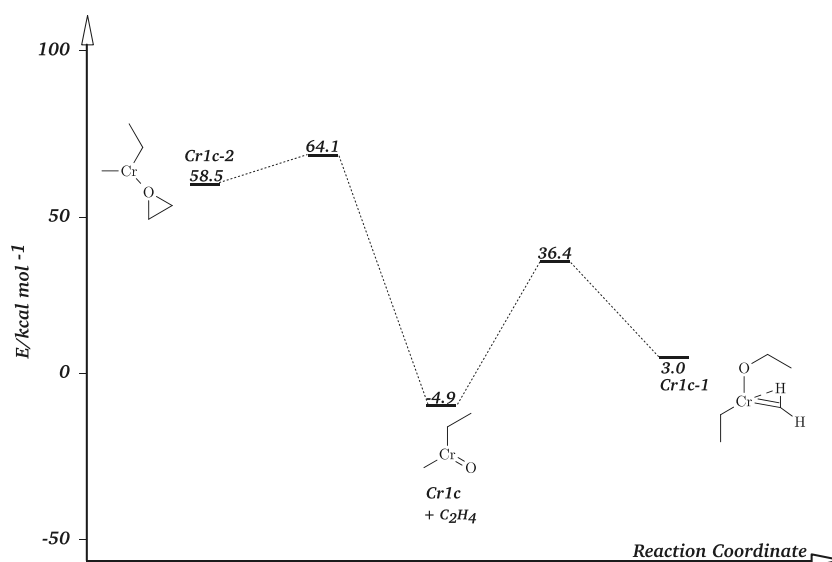


Fig. 7. Calculated reaction profile for the addition of ethylene to $(\text{O}=\text{Cr}(\text{CH}_3)(\text{CH}_2\text{CH}_3))$ ($\text{Cr1c} + \text{C}_2\text{H}_4$) at B3LYP/II//B3LYP/I + ZPE.

and $\text{Cr1} + \text{C}_2\text{H}_4 \rightarrow \text{Cr1-6}$ are thermodynamically slightly more favorable than the analogous reactions of Mo1 but the activation barriers for the former reactions are very high which makes it unlikely that they play a role for olefin addition reactions.

Fig. 7 shows the theoretically predicted reaction profile for the ethylene addition to Cr1c . Only two pathways were found and they have rather high activation barriers. The formal [1+2] addition reaction $\text{Cr1c} + \text{C}_2\text{H}_4 \rightarrow \text{Cr1c-2}$ yields a chromium-bonded oxetane complex which is much higher in energy than the educts. Finally, the attack of ethylene towards the oxygen atom may also take place with concomitant hydrogen migration $\text{Cr1c} + \text{C}_2\text{H}_4 \rightarrow \text{Cr1c-1}$ which yields a vinyliden complex that has agostic interac-

tions of one terminal C–H bond with the metal. Both reactions cannot energetically compete the previously discussed ethylene additions to Cr1 yielding Cr1-4a/b , Cr1-1 and Cr1-2 due to kinetical and thermodynamical reasons. For the formal [2+2] addition across the $\text{Cr}=\text{O}$ double bond to Cr1c , we found no direct transition state. But a multi-step mechanism will be discussed later on.

We searched for reaction pathways for the addition of ethylene to Cr1g . The results are displayed in Fig. 8. Two possible reaction pathways containing a hydrogen migration are displayed on the left-hand side. On the right hand side the side-on attack of ethylene to the chromium atom yielding the metallacyclopropane Cr1g-1 and its subsequent isomerizations are shown. The reactions

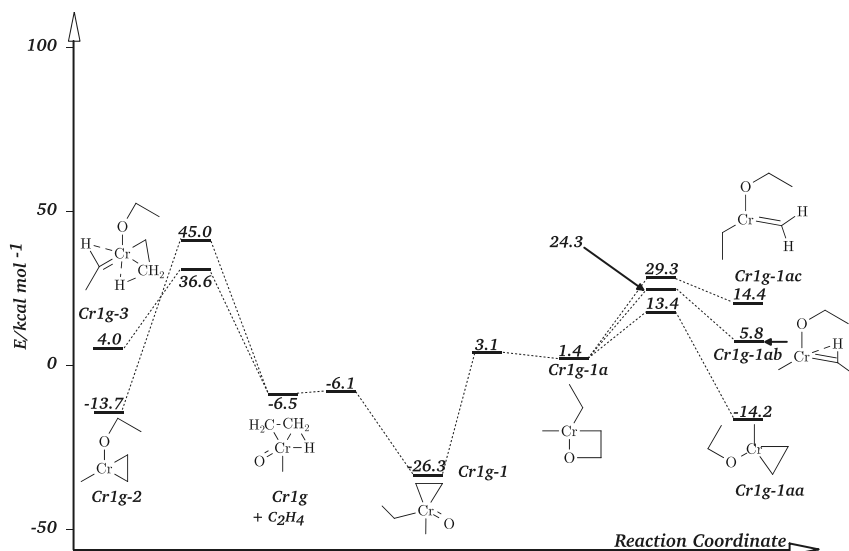


Fig. 8. Calculated reaction profile for the addition of ethylene to $(\text{O}=\text{Cr}(\text{CH}_2\text{CH}_2\text{H})(\text{CH}_3))$ ($\text{Cr1g} + \text{C}_2\text{H}_4$) at B3LYP/II//B3LYP/I + ZPE.

$\text{Cr1g} + \text{C}_2\text{H}_4 \rightarrow \text{Cr1g-2}$ and $\text{Cr1g} + \text{C}_2\text{H}_4 \rightarrow \text{Cr1g-3}$ are quite interesting: The thermodynamically preferred adduct (Cr1g-2) is kinetically disfavoured over the less stable product (Cr1g-3). Both reactions should not play a role for the reactivity of Cr1g since the reaction $\text{Cr1g} \rightarrow \text{Cr1g-1}$ which is exothermic by 19.8 kcal/mol occurs with essentially no barrier. The complete multi-step reaction from Cr1g to Cr1g-1 and its structure are shown in more detail in Fig. 10 which will be discussed later on. We found several pathways for rearrangement of Cr1g-1 yielding the high-energy isomers Cr1g-1a , Cr1g-1aa , Cr1g-1ab and Cr1g-1ac which are shown on the right-hand side of Fig. 8. Since none of them leads to a more stable isomer than Cr1g-1 they do not need to be discussed in detail.

The final isomer of Cr1 which needs to be considered for the reactivity with olefins is Cr1b . Fig. 9 shows the theoret-

ically predicted pathways for the ethylene addition to Cr1b . It becomes obvious that the side-on addition with concomitant hydrogen migration $\text{Cr1b} + \text{C}_2\text{H}_4 \rightarrow \text{Cr1g-1}$ which yields the same product as the ethylene addition to Cr1g is the only reaction that should take place in the gas phase. The latter reaction has a small activation barrier of 2.2 kcal/mol and it is exothermic by 17.9 kcal/mol. The side-on attack of ethylene to the oxygen atom $\text{Cr1b} + \text{C}_2\text{H}_4 \rightarrow \text{Cr1b-2}$ and the end-on attacks to oxygen with concomitant hydrogen migrations $\text{Cr1b} + \text{C}_2\text{H}_4 \rightarrow \text{Cr1b-1}$ and $\text{Cr1b} + \text{C}_2\text{H}_4 \rightarrow \text{Cr1g-2}$ have much higher barriers and are either endothermic or less exothermic than the previous reaction.

Fig. 10 displays the most favorable reaction pathway for ethylene addition to Cr1 which after prior rearrangement $\text{Cr1} \rightarrow \text{Cr1c} \rightarrow \text{Cr1g}$ yields the chromium ethylene complex

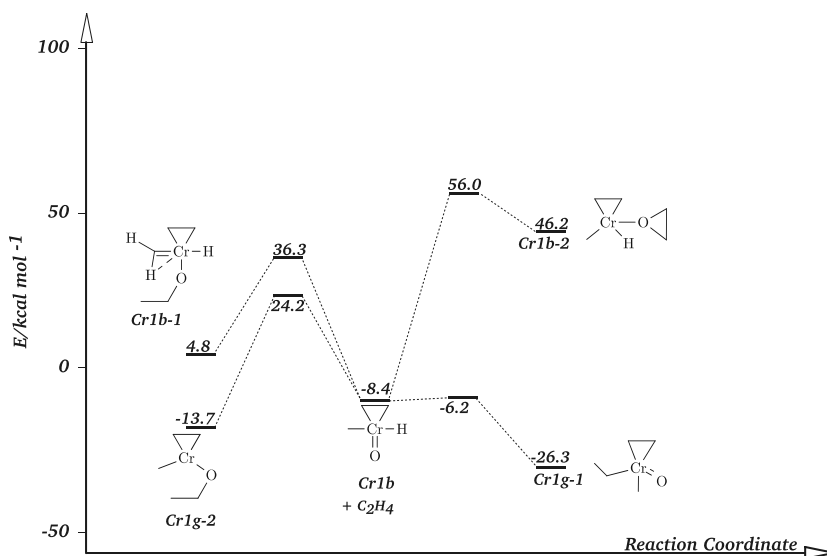


Fig. 9. Calculated reaction profile for the addition of ethylene to $(\text{O}=\text{Cr}(\text{CH}_2\text{CH}_2)(\text{H})(\text{CH}_3))$ ($\text{Cr1b} + \text{C}_2\text{H}_4$) at B3LYP/II//B3LYP/I + ZPE.

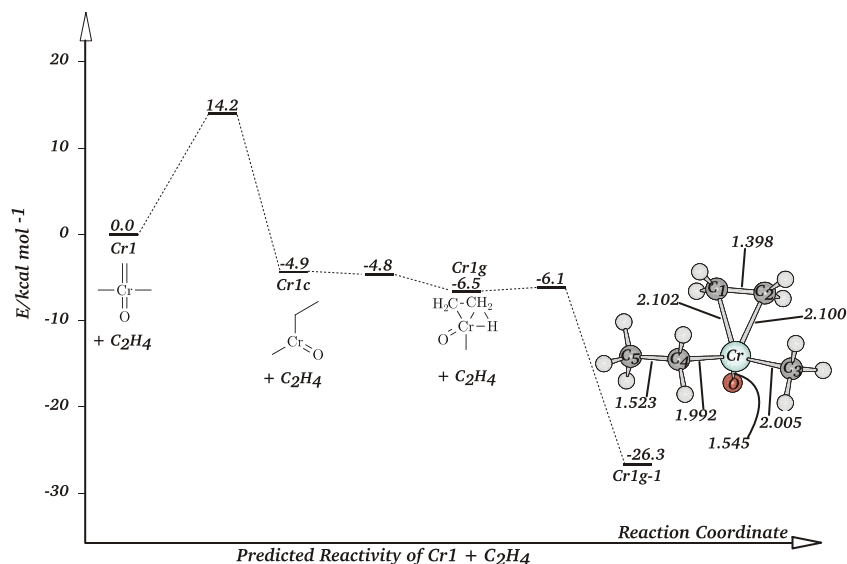


Fig. 10. Detailed reaction profile for the energetically most favorable pathway for ethylene addition to **CrI** at B3LYP/II//B3LYP/I + ZPE.

CrIg-1. Since the latter complex is the thermodynamically most stable reaction product which was found in our study we show the calculated bond lengths. The rather long Cr–C(ethylene) distance and the short H₂C–CH₂ bond indicates that **CrIg-1** should be considered a π -complex rather than a metallacyclic species [21].

4. Comparison of the group-6 elements

The calculated reaction pathways clearly show that the chromium compound **CrI** is predicted to react with ethylene in a different way than the molybdenum compound **MoI**. In this section we compare the most important reaction steps of the chromium and molybdenum system with the data for the tungsten compound **WI** which have been reported by us in a previous study [8]. Table 1 shows first the calculated activation barriers ΔE_A and reaction energies ΔE_R for rearrangement of **M1** (M = Cr, Mo, W) yielding the isomers **M1a–M1e**. Table 2 gives the ΔE_A and ΔE_R values for the addition reactions of ethylene. Note that the latter reactions may involve either prior or concomitant rearrangement of the metal compound.

The lowest activation barrier for rearrangement of the chromium compound is the reaction **CrI** → **CrIc** which involves a change of the formal oxidation state from Cr(VI) to Cr(IV). The rearrangement which leads to the formation of **CrIb** has the same activation barrier because it consists of a multiple-step process **CrI** → **CrIc** → **CrIg** → **CrIb** where the first step has the highest barrier (Fig. 4). The formation of **CrIg** is not discussed because it is a very shallow energy minimum. The formation of **CrIb** and **CrIc** are the only rearrangements of **CrI** which are exothermic (Table 1). The analogous rearrangements of the molybdenum and tungsten compounds **M1** → **M1b** and **M1** → **M1c** (M = Mo, W) have much higher barriers and are thermodynamically less favorable than the reactions of the chromium system. Note that the reaction **M1** → **M1b** for molybdenum and tungsten is a single-step process unlike the chromium compound.

Table 2 shows that the [2+2]_{M,C} addition of ethylene across the M=C double bond has for all three metals a much lower barrier than the [3+2]_{C,O} addition. There is a distinct difference between the chromium system on the one hand side and the molybdenum and tungsten

Table 1

Calculated reaction energies (ΔE_R) and activation energies (ΔE_A) for the isomerization reactions of (O=)Mo(=CH₂)(CH₃)₂ (**Mo1**) and (O=)Cr(=CH₂)(CH₃)₂ (**Cr1**) in comparison with the corresponding tungsten system (O=)W(=CH₂)(CH₃)₂ (**W1**) at B3LYP/II//B3LYP/I + ZPE

Structure	(O=)Cr(=CH ₂)(CH ₃) ₂		(O=)Mo(=CH ₂)(CH ₃) ₂		(O=)W(=CH ₂)(CH ₃) ₂	
	(Cr1)		(Mo1)		(W1) ^a	
	ΔE_R	ΔE_A	ΔE_R	ΔE_A	ΔE_R	ΔE_A
M1a	14.9	43.2	51.6	69.1	63.9	80.1
M1b	−8.4	14.2 ^b	−1.6	48.9	4.5	49.8
M1c	−4.9	14.2	21.4	34.5	29.4	41.6
M1d	23.7	56.0	23.4	61.3	26.4	62.4
M1e	14.9	49.1	16.2	53.8	22.3	56.8

All values are in kcal/mol.

^a Values taken from Ref. [8].

^b Highest barrier of a multi-step rearrangement with initial formation of **CrIc**.

Table 2

Calculated reaction energies (ΔE_R) and activation energies (ΔE_A) for the additions of ethylene to $(\text{O}=\text{M})\text{O}(\text{=CH}_2)(\text{CH}_3)_2$ (**Mo1**) and $(\text{O}=\text{Cr})(\text{=CH}_2)(\text{CH}_3)_2$ (**Cr1**) in comparison with the corresponding tungsten system $(\text{O}=\text{W})(\text{=CH}_2)(\text{CH}_3)_2$ (**W1**) at B3LYP/II//B3LYP/I + ZPE

Reaction product (reaction)	$(\text{O}=\text{Cr})(\text{=CH}_2)(\text{CH}_3)_2$ (Cr1) + C ₂ H ₄		$(\text{O}=\text{Mo})(\text{=CH}_2)(\text{CH}_3)_2$ (Mo1) + C ₂ H ₄		$(\text{O}=\text{W})(\text{=CH}_2)(\text{CH}_3)_2$ (W1) + C ₂ H ₄ ^a	
	ΔE_R	ΔE_A	ΔE_R	ΔE_A	ΔE_R	ΔE_A
M1-1 ([3+2] _{C,O})	-4.3	32.6	25.6	44.2	37.0	52.5
M1-4a ([2+2] _{M,C})	1.2	14.7	-0.6	8.4	-1.1	9.5
M1-7 ([2+2] _{M,O})	35.1	36.7	28.0	32.9	29.9	33.4
M1-2 ([1+2] _C)	-2.1	23.7	23.7	45.5	30.3	56.8
M1g-1 ([1+2] _M) ^b	-26.3	14.2	-19.2	34.5	-15.2	41.6
M1-6 (O) ^c	13.1	43.9	12.8	45.6	15.6	46.6
M1-3 (O) ^c	-4.0	60.7	25.9	71.0	38.5	78.4
M1-5 (O) ^c	2.5	34.4	4.4	36.2	10.6	39.5

All values are in kcal/mol.

The most favorable pathways are given in *italics*.

^a Values taken from Ref. [8] except for the data for **W1g-1** which are from more recent calculations by us.

^b The [1+2] addition to the metal takes place after multiple-step rearrangements **M1** → **M1g-1**. The first rearrangement **M1** → **M1c** has the highest activation barrier.

^c Ethylene addition to the terminal oxo group with concomitant hydrogen migration.

compounds on the other side. The [2+2]_{M,C} addition is the overall kinetically most favored reaction for M = Mo and W which has rather low barriers of 8.4 kcal/mol (Mo) and 9.5 kcal/mol (W). The latter reactions are nearly thermoneutral while the [3+2]_{C,O} addition has not only much higher barriers but it is also strongly endothermic. In case of chromium the [3+2]_{C,O} addition has a higher barrier than the [2+2]_{M,C} addition but the former reaction is exothermic and thus, it is thermodynamically favored over the latter process.

The lowest activation energy for ethylene addition to **Cr1** is predicted for the multiple-step reaction **Cr1** → **Cr1c** → **Cr1g** (+C₂H₄) → **Cr1g-1** (Fig. 10) where the highest barrier comes from the initial rearrangement **Cr1** → **Cr1c**. The final [1+2]_M addition leads to the energetically lowest lying product which was found in our work. The reaction cascade is kinetically and thermodynamically favored over all other reactions which were studied by us (Table 2). We calculated the analogous reaction for molybdenum and tungsten where the initial rearrangement **M1** → **M1c** has much higher barriers than for the chromium system (Table 1). The following steps **M1c** → **M1g** → **M1g-1** (M = Mo, W) have lower barriers than the initial rearrangement but the rather large activation energies for the first step which are much higher than for the [2+2]_{M,C} addition let it seem unlikely that the [1+2]_M addition takes place, although it is the thermodynamically most favored reaction (Table 2).

5. Summary and conclusion

The results of this work can be summarized as follows.

The kinetically most favorable reaction pathway for ethylene addition to $\text{MoO}(\text{CH}_3)_2(\text{CH}_2)$ (**Mo1**) is the [2+2]_{M,O} addition across the Mo=CH₂ double bond which has an activation barrier of only 8.4 kcal/mol. The reaction is

slightly exothermic with $\Delta E_R = -0.6$ kcal/mol. The [2+2]_{M,O} addition across the Mo=O double bond and the [3+2]_{C,O} addition have much higher barriers and are strongly endothermic. The thermodynamically most favored reaction is the [1+2]_M addition of ethylene to the metal atom which takes place after prior rearrangement of the Mo(VI) compound **Mo1** to the Mo(IV) isomer **Mo1g**. The reaction is -19.2 kcal/mol exothermic but it has a large barrier of 34.5 kcal/mol.

The kinetically and thermodynamically most favorable reaction pathway for ethylene addition to the chromium homologue $\text{CrO}(\text{CH}_3)_2(\text{CH}_2)$ (**Cr1**) is the multiple-step process with initial rearrangements **Cr1** → **Cr1c** → **Cr1g** which are followed by a [1+2]_{Cr} addition yielding an ethylene π complex **Cr1g** → **Cr1g-1**. The highest barrier comes from the first step **Cr1** → **Cr1c** which has an activation energy of 14.2 kcal/mol. The overall reaction is exothermic by -26.3 kcal/mol.

The comparison of the group-6 elements shows that the molybdenum and tungsten compounds **Mo1** and **W1** have a similar reactivity while the chromium compound has a much more diverse reactivity pattern.

We want to point out that the focus of the present work is a comparison of the singlet potential energy surfaces for the reaction of the group-6 oxo compounds with ethylene. It is likely that triplet or even higher spin states may play a role particularly for the chromium species. The investigation of the triplet state has not been considered in this work.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.12.008.

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