



Comparative theoretical study of [3+2] and [2+2] cycloadditions of ethylene and $WXYMe_2$; X, Y = (=O), (=NH), (=CH₂)[☆]

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ABSTRACT

Quantum chemical calculations employing density functional theory (B3LYP) were carried out to compare the preference of [3+2] versus [2+2] cycloadditions of ethylene to $WO_2(CH_3)_2$ (**W2**), $WONH(CH_3)_2$ (**W3**), $WNHCH_2(CH_3)_2$ (**W4**), $W(CH_2)_2(CH_3)_2$ (**W5**), and $W(NH)_2(CH_3)_2$ (**W6**). The results are compared to previously published data on the related tungsten complex $WOCH_2(CH_3)_2$ (**W1**). In agreement with $MoOCH_2(CH_3)_2$ and $ReO_2CH_3CH_2$, all six tungsten complexes prefer a [2+2] pathway rather than a [3+2] cycloaddition which is the reverted preference compared to the analogous compounds $TcO_2CH_3CH_2$, $MnO_2CH_3CH_2$, RuO_3CH_2 , OsO_3CH_2 and $OsO_2(NH)_2$, and $MO_2CH_3CH_2$ (M = Ir, Rh, Co).

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1. Introduction

The mechanism of the *cis*-dihydroxylation of olefins with OsO_4 is now well established after a controversy about two alternative pathways was finally solved with the help of quantum chemical investigations. Originally, a concerted [3+2] cycloaddition was proposed [1] while an alternative two-step pathway with initial [2+2] addition with subsequent rearrangement was later suggested [2]. Both pathways yield an osma-2,5-dioxolane as final product. It was shown that the initial [2+2] cycloaddition has a significantly higher barrier than the [3+2] pathway [3]. Other metal oxides like RuO_4 and ReO_4^- were also predicted to prefer a [3+2] cycloaddition rather than a [2+2] reaction [4,5]. A study by Deubel and Muñiz showed that the pathway via [3+2] cycloaddition is still preferred for ethylene addition to $OsO_2(NH)_2$ [6]. The authors predicted a decrease of the activation energies in the order $O/O > O/NH > NH/NH$.

A different scenario is theoretically predicted when a metal-carbon double bond is involved: the [2+2] addition of ethylene across the $M=C$ alkylidene bond becomes competitive with the [3+2] reaction for OsO_3CH_2 and $OsO_2(CH_2)_2$ [7,8] and the former reaction becomes favored over the latter for $ReO_2CH_3CH_2$ [9], $WO(CH_3)_2CH_2$, $MoO(CH_3)_2CH_2$, and $CrO(CH_3)_2CH_2$ [10]. The [3+2] cycloaddition of ethylene is preferred for $TcO_2CH_3CH_2$ [11],

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RuO_3CH_2 [12], $IrO_2CH_3CH_2$, $RhO_2CH_3CH_2$, and $CoO_2CH_3CH_2$ [13]. Experimentally, Schrock reported the synthesis of $RR'W(=NAr)$ ($=CHCMe_3$) and he showed that the reaction of the latter with ethylene yields $RR'W(=NAr)(=CH_2)$ and $H_2C=CHCMe_3$ which indicates that a [2+2] addition across the $W=CHCMe_3$ double bond has taken place [14]. As part of our ongoing theoretical work about the reaction mechanism of olefin addition to metal=E double bonds [3a,4a,b,5,7–13] we present a comparative study of [2+2] and [3+2] ethylene additions to $W(=O)_2(CH_3)_2$ (**W2**), $(O=)W(=NH)(CH_3)_2$ (**W3**), $(H_2C=)W(=NH)(CH_3)_2$ (**W4**), $(H_2C=)W(=CH_2)(CH_3)_2$ (**W5**) and $(HN=)W(=NH)(CH_3)_2$ (**W6**). We compare the results with our previously published data for the ethylene addition to $(O=)W(=CH_2)(CH_3)_2$ (**W1**) [10a], its lighter homologs [10b], and similar group-7 [9,11], group-8 [7,8,12], and group-9 [13] compounds. Due to the diversity of the compounds, we only consider [3+2] and [2+2] pathways. Therefore, we can not exclude that other pathways play an important role for ethylene addition to these complexes. The aim of this work is to elucidate the preference of the metal compounds for a [3+2] or a [2+2] addition reaction.

2. Methods

All geometry optimizations were carried out using hybrid density functional theory (DFT) employing the B3LYP hybrid functional [15] as implemented [16] in the GAUSSIAN 03 program [17] without any symmetry constraints. Ahlrichs' triple zeta basis set (TZVP) [18] was used for the elements O, N, C and H. For tungsten, the Stuttgart/Köln relativistic effective core potential (ECP) replacing

60 core electrons was employed in combination with a (311111/22111/411) [19] 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) [20] calculations were carried out to ensure the connectivity of the minima and transition states. 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) [21] were used for the elements O, N, C and H. The tungsten basis set is augmented by two sets of *f* and one set of *g* functions derived by Martin and Sundermann [22]. 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. This is consistent and directly comparable with our previously published data.

3. Results and discussion

The focus of this work lies on the energetics of the [2+2] and [3+2] cycloadditions rather than the geometries of the compounds. Therefore, we discuss only the reaction energies and activation barriers but not the geometries of the calculated species. A full set of cartesian coordinates and energies of all compounds is given as Supporting information.

Fig. 1 shows the possible [3+2] and [2+2] cycloadditions. On the right hand side of Fig. 1, the [2+2] cycloaddition $W2 + C_2H_4 \rightarrow W2-1$ with a rather high barrier is shown. The highly endothermic [3+2] pathway $W2 + C_2H_4 \rightarrow W2-2$ is shown on the left hand side. The [2+2] addition is favored over the [3+2] pathway but both are yielding endothermic products.

For the system $W3 + C_2H_4$, one [3+2] cycloaddition and two [2+2] cycloadditions are possible. They are presented in Fig. 2. All three cycloaddition pathways are endothermic. The [2+2] addition across the $W=NH$ double bond $W3 + C_2H_4 \rightarrow W3-1$ has the lowest barrier and is only slightly endothermic. The other possible [2+2] cycloaddition pathway across the $W=O$ double bond $W3 + C_2H_4 \rightarrow W3-2$ is more endothermic and has a higher barrier. Finally, there is the [3+2] pathway $W3 + C_2H_4 \rightarrow W3-3$ which has the highest activation barrier and the highest endothermicity of all considered reactions.

The picture changes slightly for ethylene addition to $W4$. The calculated reaction profile is shown in Fig. 3. The [3+2] cycloaddition $W4 + C_2H_4 \rightarrow W4-3$ is still endothermic and has a high barrier

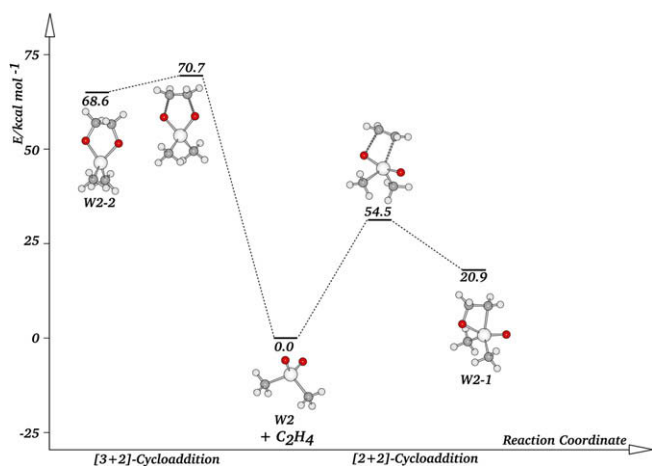


Fig. 1. Calculated reaction profile for the cycloaddition reactions of ethylene and $(O=)_2W(CH_3)_2$ ($W2$) at B3LYP/II//B3LYP/I+ZPE.

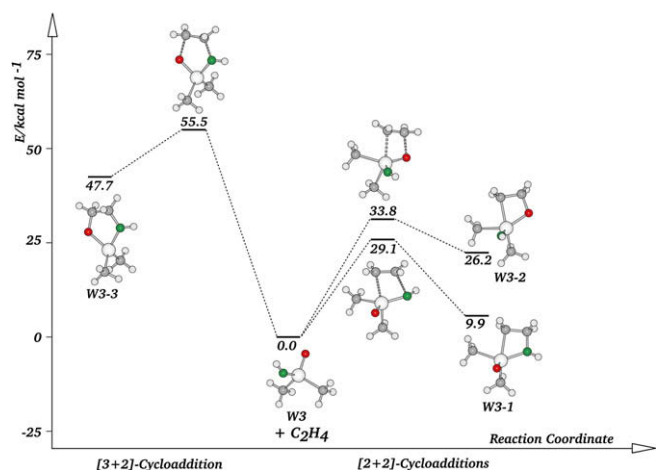


Fig. 2. Calculated reaction profile for the cycloaddition reactions of ethylene and $(O=)W(=NH)(CH_3)_2$ ($W3$) at B3LYP/II//B3LYP/I+ZPE.

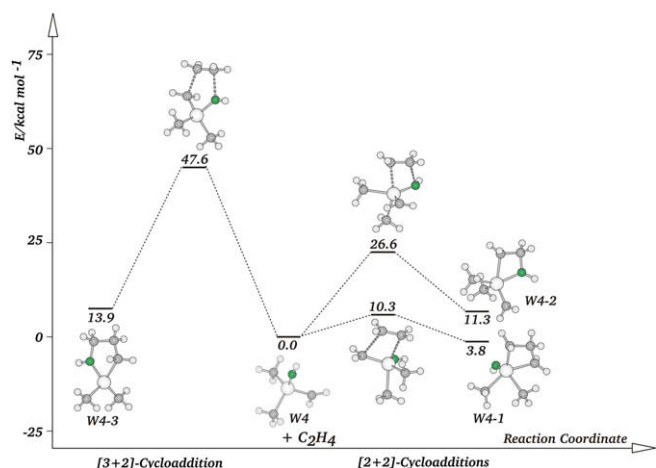


Fig. 3. Calculated reaction profile for the cycloaddition reactions of ethylene and $(H_2C=)W(=NH)(CH_3)_2$ ($W4$) at B3LYP/II//B3LYP/I+ZPE.

but the endothermicity of the process $W4 + C_2H_4 \rightarrow W4-2$ is comparable to the latter even though the barrier is significantly lower. This implies that the formal $W(VI)$ species $W4-2$ is energetically nearly degenerate to the $W(IV)$ compound $W4-3$. The [2+2] cycloaddition across the $W=CH_2$ double bond $W4 + C_2H_4 \rightarrow W4-1$ has the lowest barrier and is nearly thermoneutral.

$W5$ exhibits a different reactivity with olefins which is shown in Fig. 4. The [2+2] cycloaddition $W5 + C_2H_4 \rightarrow W5-1$ has a low barrier and is slightly exothermic. To the formal [3+2] cycloaddition product $W5-1b$, no direct transition state was found but it is accessible via the nearly thermoneutral rearrangement $W5-1 \rightarrow W5-1b$. Again, we have the situation that the formal $W(IV)$ compound $W5-1b$ is energetically nearly degenerate to formal $W(VI)$ species. Here, the $W(VI)$ compounds are $W5$ and $W5-1$. Finally, $W5-1$ can undergo another rearrangement into another [2+2] cycloaddition product $W5-1a$. The connectivity of the atoms is the same but $W5-1a$ is slightly lower in energy than $W5-1$. The associated barrier is negligible. Such a scenario was reported by us also for the system $W1 + C_2H_4$ [10a].

Fig. 5 shows the calculated cycloadditions for the system $W6 + C_2H_4$. On the left hand side of Fig. 5 the endothermic [3+2] pathway $W6 + C_2H_4 \rightarrow W6-2$ is shown. It has a rather high barrier. The alternative [2+2] addition of ethylene to $W6$ yielding $W6-1$ has a significantly lower barrier and a lower endothermicity.

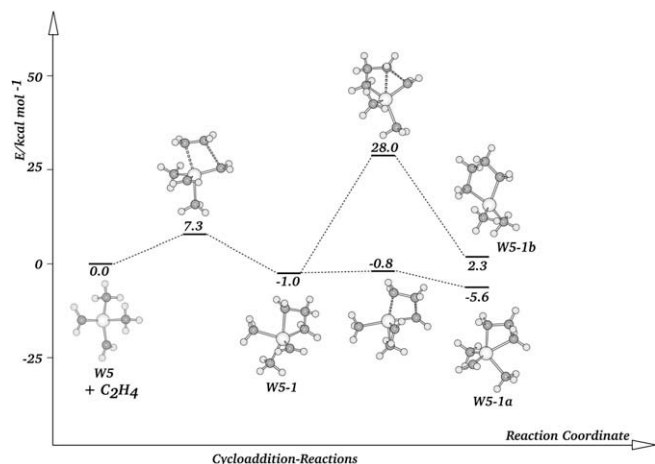


Fig. 4. Calculated reaction profile for the cycloaddition reactions of ethylene and $(\text{H}_2\text{C}=\text{C})_2\text{W}(\text{CH}_3)_2$ (**W5**) at B3LYP/II//B3LYP/I+ZPE.

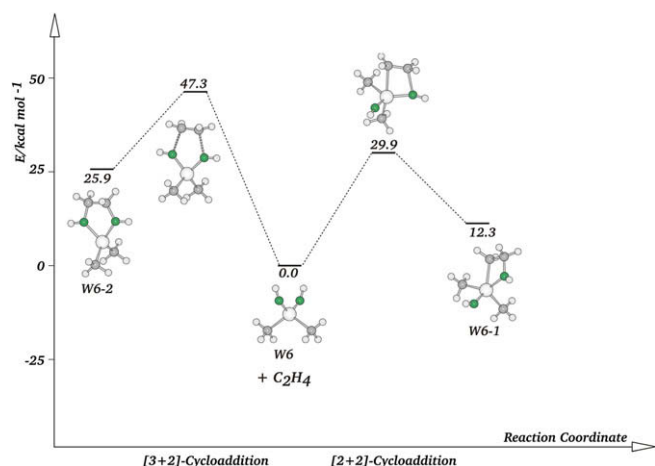


Fig. 5. Calculated reaction profile for the cycloaddition reactions of ethylene and $(\text{HN}=\text{C})_2\text{W}(\text{CH}_3)_2$ (**W6**) at B3LYP/II//B3LYP/I+ZPE.

The studied systems exhibit differences but also similarities in their reactivity with olefins. Table 1 compiles the reaction energies (ΔE_R) and activation energies (ΔE_A) for the possible [2+2] and [3+2] additions of ethylene to **W1**–**W6**. The favored pathway is indicated by numbers in italics. Note that some of the presented reactions

may involve subsequent rearrangements of the metal compound. In these cases, the highest barrier is given.

Our previously published results [10a] on the system **W1** + C_2H_4 agree best with **W5** + C_2H_4 for the [2+2] cycloaddition across the $\text{W}=\text{CH}_2$ double bond. The [2+2] ethylene addition to **W5** is predicted to have a slightly lower barrier and to be more exothermic than ethylene addition to **W1**. The substitution pattern NH/CH_2 seems to enlarge the $[2+2]_{\text{WC}}$ barrier slightly. Additionally, the slightly exothermic reaction for **W1** turns into an endothermic process for **W4**. The [3+2] cycloaddition of the system **W1** + C_2H_4 is quite different from those presented here because it is a pathway where $\text{W}=\text{O}$ and $\text{W}=\text{CH}_2$ double bonds are involved but it is quite similar to **W3** + C_2H_4 where the addition involves $\text{W}=\text{O}$ and $\text{W}=\text{NH}$ double bonds. In all considered systems **W1**–**W6** the [2+2] addition is clearly favored over the alternative [3+2] pathway. For the similar systems $\text{TcO}_2\text{CH}_2\text{CH}_3$, $\text{MnO}_2\text{CH}_2\text{CH}_3$, RuO_3CH_2 , OsO_3CH_2 , $\text{OsO}_2(\text{NH})_2$, and $\text{MO}_2\text{CH}_2\text{CH}_3$ ($\text{M} = \text{Ir}, \text{Rh}, \text{Co}$) the reverted preference was observed [3a,6,11–13]. $\text{ReO}_2\text{CH}_2\text{CH}_3$ and $\text{MoOCH}_2(\text{CH}_3)_2$ on the other side prefer the [2+2] cycloaddition like the six tungsten complexes **W1**–**W6** [9,10b,11].

4. Summary

The kinetically favored ethylene addition to **W2** is the [2+2] pathway across the $\text{W}=\text{O}$ double bond. The barrier is still rather high ($\Delta E_A = 54.5$ kcal/mol) and the process is endothermic by 20.9 kcal/mol. For the system **W3** + C_2H_4 , the [2+2] addition across the $\text{W}=\text{NH}$ double bond is favored over the alternative cycloadditions although it is still endothermic. The ethylene addition to **W4** clearly favors the [2+2] addition where the $\text{W}=\text{CH}_2$ double bond is involved. For the system **W5** + C_2H_4 , the [2+2] pathway across the $\text{W}=\text{CH}_2$ double bond becomes slightly exothermic ($\Delta E_A = -4.6$ kcal/mol). The associated barrier is quite small with 7.3 kcal/mol. The activation energy is slightly lower and the exothermicity is slightly higher compared to the system **W1** + C_2H_4 . The kinetically favored ethylene addition to **W6** is the $[2+2]_{\text{WN}}$ pathway. The alternative $[3+2]_{\text{NN}}$ cycloaddition has a higher barrier and also a higher endothermicity.

The presented calculations show that the activation barriers of the favored [2+2] cycloadditions decrease in the order $\text{O}/\text{O} > \text{NH}/\text{NH} \approx \text{O}/\text{NH} > \text{NH}/\text{CH}_2 \approx \text{O}/\text{CH}_2 > \text{CH}_2/\text{CH}_2$. For the reaction energies the order is only slightly different: $\text{O}/\text{O} > \text{NH}/\text{NH} > \text{O}/\text{NH} > \text{NH}/\text{CH}_2 > \text{O}/\text{CH}_2 \approx \text{CH}_2/\text{CH}_2$. The preference towards [2+2] or [3+2] cycloaddition depends mainly on the transition metal while the substituents are less important.

Table 1

Calculated reaction energies (ΔE_R) and activation energies (ΔE_A) for the cycloaddition reactions of $(\text{O}=\text{C})_2\text{W}(\text{CH}_3)_2$ (**W2**), $(\text{O}=\text{C})\text{W}(\text{NH})(\text{CH}_3)_2$ (**W3**), $(\text{HN}=\text{C})\text{W}(\text{CH}_2)(\text{CH}_3)_2$ (**W4**), $(\text{H}_2\text{C}=\text{C})_2\text{W}(\text{CH}_3)_2$ (**W5**), $(\text{HN}=\text{C})_2\text{W}(\text{CH}_3)_2$ (**W6**) in comparison with the corresponding oxo carbene system $(\text{O}=\text{C})\text{W}(\text{CH}_2)(\text{CH}_3)_2$ (**W1**) at B3LYP/II//B3LYP/I+ZPE. All values are in kcal/mol. The most favorable pathway is given in *italics*.

| Cycloaddition | O/CH ₂ W1 ^a | | O/O W2 | | O/NH W3 | | NH/CH ₂ W4 | | CH ₂ /CH ₂ W5 | | NH/NH W6 | |
|---------------------|---------------------------------------------|------------------|------------------|--------------|-------------------|--------------|---------------------------------|--------------|-----------------------------------------------|-------------------|--------------------|--------------|
| | ΔE_R | ΔE_A | ΔE_R | ΔE_A | ΔE_R | ΔE_A | ΔE_R | ΔE_A | ΔE_R | ΔE_A | ΔE_R | ΔE_A |
| [2+2] _{WO} | 29.9 | 33.4 | 20.9 | 54.5 | 26.2 | 33.8 | – | – | – | – | – | – |
| [2+2] _{WN} | – | – | – | – | 9.9 | 29.1 | 11.3 | 26.6 | – | – | 12.3 | 29.9 |
| [2+2] _{WC} | –1.9 | 9.5 ^b | – | – | – | – | 3.8 | 10.3 | –4.6 | 7.3 ^b | – | – |
| [3+2] _{OO} | – | – | 68.6 | 70.7 | – | – | – | – | – | – | – | – |
| [3+2] _{ON} | – | – | – | – | 47.7 | 55.5 | – | – | – | – | – | – |
| [3+2] _{NN} | – | – | – | – | – | – | – | – | – | – | 25.9 | 47.3 |
| [3+2] _{CO} | 37.0 | 52.5 | – | – | – | – | – | – | – | – | – | – |
| [3+2] _{CN} | – | – | – | – | – | – | 13.9 | 47.6 | – | – | – | – |
| [3+2] _{CC} | – | – | – | – | – | – | – | – | 2.3 | 28.0 ^b | – | – |

^a Values taken from Ref. [8].

^b Two-step pathway where the highest barrier is given.

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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.2009.08.022.

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