Theoretical Study of Ethylene Addition to $O=W(=CH_2)(CH_3)_2$

Robin Haunschild and Gernot Frenking

Fachbereich Chemie der Philipps-Universität Marburg, Hans-Meerwein-Straße,
35043 Marburg, Germany

Reprint requests to Prof. Dr. G. Frenking, E-mail: Frenking@chemie.uni-marburg.de

Dedicated to Prof. Helgard G. Raubenheimer on the occasion of his 65th birthday

Quantum chemical calculations using density functional theory at the B3LYP level of theory were carried out to investigate the reaction pathways for the addition of ethylene to $WO(CH_3)_2(CH_2)$ (**W1**). The results are compared to those of previous theoretical studies of the ethylene addition to $OsO_3(CH_2)$ (**Os1**) and $ReO_2(CH_3)(CH_2)$ (**Re1**). The theoretically predicted reactions pathways exhibit significant differences. The energetically most favourable reaction of the tungsten system **W1** is the $[2+2]_{W,C}$ addition across the W=C double bond yielding the metallacyclobutane **W3a** which then rearranges to the slightly more stable isomer **W3b**. The $[2+2]_{Re,C}$ addition of the rhenium compound yielding the metallacyclobutane **Re3a** has the lowest activation barrier for the ethylene addition to the rhenium system, but the reaction is endothermic while the exothermic formation of the more stable isomer **Re3b** has a much higher activation barrier. The $[3+2]_{C,O}$ addition $\mathbf{Os1} + C_2H_4 \rightarrow \mathbf{Os2}$ is the thermodynamically most favorable reaction of the osmium compound.

Key words: Reaction Mechanism, DFT Calculations, Oxo Carbene Complexes, Cycloaddition, Metallacycle

Introduction

Various theoretical studies [1] have shown that the addition of olefins to OsO_4 initiates with a concerted [3+2] reaction rather than through a two-step process with initial [2+2] addition across an Os=O double bond. Subsequent work [2] has indicated that other metal oxides such as RuO_4 and ReO_3^- also prefer a [3+2] mechanism over a [2+2] reaction [3]. The introduction of an imido group in $OsO_2(NH)_2$ does not change the overall profile of the reaction. Deubel and Muñiz [4] reported that the three [3+2] addition reactions of ethylene which are possible for the system are clearly favoured over the [2+2] reactions. The authors predicted that the calculated activation barriers decrease with the order O/O > O/NH > NH/NH.

The situation becomes different when a metal-carbene double bond is involved in the reaction with an olefin. It has recently been shown by us that the [2+2] addition of ethylene to $OsO_2(CH_2)_2$, $OsO_3(CH_2)$, and $ReO_2(CH_3)(CH_2)$ becomes competitive or even more favorable than the [3+2] reaction [5–7]. The calculated reaction profiles were found to be significantly more complicated than those for the ethylene addition to binary metal oxides, because the C-C and C-O ring closure can lead to energetically low lying intermediates. We extended our theoretical investigations to group-6 compounds, because tungsten and molybdenum are the only transition metals besides rhenium for which oxo carbenes are experimentally known [8]. To this end we theoretically investigated the reaction course for the addition of ethylene to $WO(CH_3)_2(CH_2)$ which is a model compound for $WO(tBuCH_2)_2[CtBu(SiPh_2tBu)]$. The latter molecule was synthesized by an unusual silyl migration and consecutive treatment with O_2 [9].

In this paper, we present our theoretical results of the reaction pathways for the addition of ethylene to $WO(CH_3)_2(CH_2)$ and compare them to the recently published data of the related ethylene addition to $OsO_3(CH_2)$ and $ReO_2(CH_3)(CH_2)$ [7].

Computational Methods

All geometry optimizations were carried out without any symmetry constraints using gradient corrected density functional theory (DFT) employing the B3LYP hybrid functional [10] as implemented [11] in the Gaussian 03 program [12]. For the elements C, H and O, Ahlrichs' TZVP basis set [13] was used. For Os, Re and W, the Stuttgart/Köln relativistic effective core potential (ECP) replacing 60 core electrons was em-
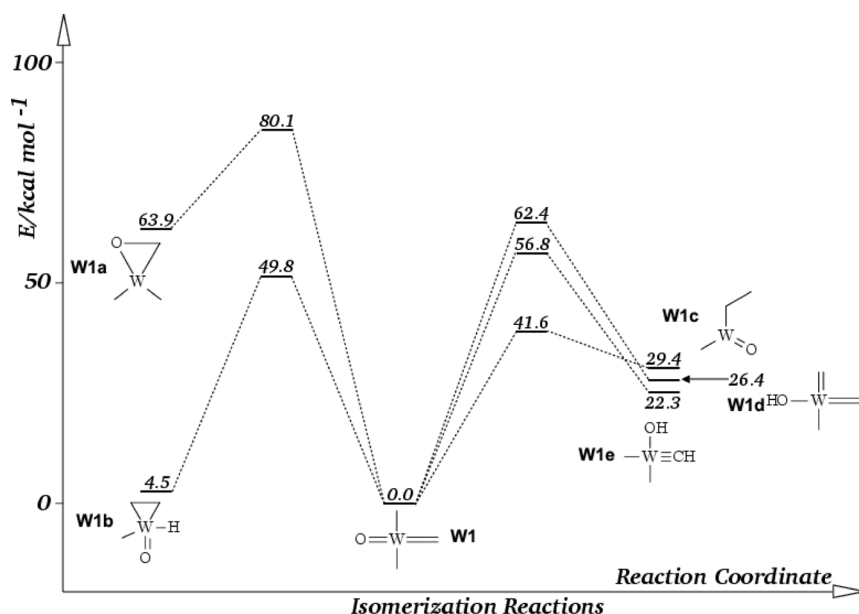
Fig. 1. Calculated reaction coordinate for the isomerizations of WO(CH$_3$)$_2$(CH$_2$) (**W1**) at B3LYP/II//B3LYP/I+ZPE.

ployed in combination with a (311111/22111/411) valence basis set [14]. This combination is denoted here as basis set I. At all stationary points, the vibrational frequencies were calculated to verify the nature of stationary point (minimum or transition state). For every transition state, intrinsic reaction coordinate (IRC) [15] calculations were performed in order to verify the connectivity between minima and transition states. On the stationary points at the B3LYP/I level of theory, additional single point calculations were performed using a larger basis set II in conjunction with the B3LYP hybrid functional. In basis set II, the Stuttgart/Köln valence basis set is augmented by two sets of *f* functions and one set of *g* functions derived by Martin and Sundermann [16]; for the elements C, H and O, the correlation consistent cc-pVTZ basis set of Dunning [17] was used. All relative energies discussed below relate to B3LYP/II//B3LYP/I calculations and include unscaled zero point energy (ZPE) contributions. The ZPE contributions were taken from the B3LYP/I calculations.

Results and Discussion

In our previous theoretical work about ethylene addition to OsO$_2$(CH$_2$)$_2$, OsO$_3$(CH$_2$), and ReO$_2$(CH$_3$)(CH$_2$) we found that the metal compounds may rearrange to isomers which may be lower in energy than the parent system [5–7]. We therefore calculated isomers of WO(CH$_3$)$_2$(CH$_2$) (**W1**) and the as-

sociated transition states. Fig. 1 shows the calculated reaction profile for the isomerizations of **W1**.

Five isomerizations were considered, two leading to cyclic (**W1a** and **W1b**) and three leading to acyclic (**W1c** – **W1e**) isomers. All isomers **W1a** – **W1e** are higher in energy than the parent structure **W1**. The cyclic isomer **W1a** is the least stable form which is 63.9 kcal mol^{-1} higher in energy than **W1**. The activation barrier for the process **W1 → W1a** is 80.1 kcal mol^{-1}. The isomerization to the other cyclic isomer **W1b** which comprises C–C bond formation and methyl-to-metal hydrogen migration is only slightly endothermic by 4.5 kcal mol^{-1}, but the activation barrier of 49.8 kcal mol^{-1} is still quite high. The rearrangement of **W1** yielding **W1c** *via* methyl migration is the kinetically most favorable process, but the activation barrier of 41.6 kcal mol^{-1} is still prohibitively large. Furthermore, **W1c** is thermodynamically disfavored by 29.4 kcal mol^{-1}. 1,2 Hydrogen migrations from the methyl or from the methylene group yield isomers **W1d** and **W1e** which are 3.0 and 7.1 kcal mol^{-1} more stable than **W1c**, but both isomers are still 26.4 kcal mol^{-1} (**W1d**) and 22.3 kcal mol^{-1} (**W1e**) less stable than **W1**. Additionally, the substantial barriers of 62.4 kcal mol^{-1} for the reaction **W1 → W1d** and 56.8 kcal mol^{-1} for the reaction **W1 → W1e** indicate that the biscarbene (**W1d**) and hydroxo carbyne (**W1e**) isomers are unlikely to be formed under normal conditions. It is interesting
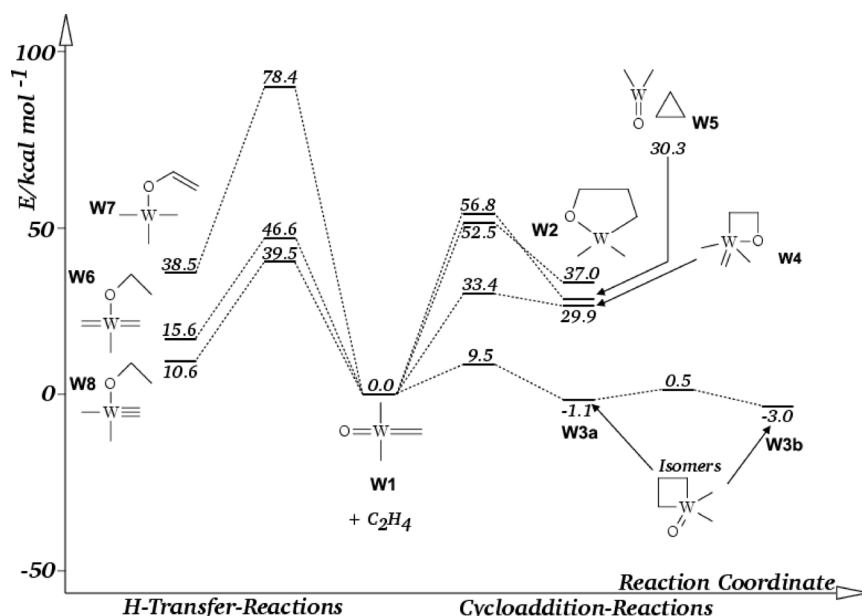
Fig. 2. Calculated reaction coordinate for the addition of ethylene to WO(CH$_3$)$_2$(CH$_2$) (**W1**) at B3LYP/II//B3LYP/I+ZPE.

to note that isomer **W1c** is slightly higher in energy than **W1d** and **W1b** but the formation of the latter species from **W1** has much higher activation barriers than the rearrangement yielding **W1c**. The calculated reaction profile shown in Fig. 1 suggests that the isomeric forms **W1a** – **W1e** should not play an important role in the ethylene addition to **W1**. We therefore focused on the reaction pathways for the reaction C$_2$H$_4$ + **W1**. The theoretically predicted reaction profile is shown in Fig. 2.

There is only one possible [3+2] pathway leading to the metallacycle **W2**. The reaction is endothermic by 37.0 kcal mol^{-1} with a substantial barrier of 52.5 kcal mol^{-1}. Fig. 2 shows two concerted [2+2] cycloadditions: one yielding **W3a** and the other yielding **W4**. The addition of C$_2$H$_4$ across the W=CH$_2$ bond of **W1** forming **W3a** is a slightly exothermic reaction by −1.1 kcal mol^{-1} with a barrier of only 9.5 kcal mol^{-1}. Consecutively, **W3a** can isomerize *via* a transition state of 0.5 kcal mol^{-1} to **W3b**. This isomerization is slightly exothermic by −1.9 kcal mol^{-1}. The second [2+2] cycloaddition of ethylene across the W=O bond of **W1** yielding **W4** is kinetically and thermodynamically much less favorable than the addition across the W=CH$_2$ bond. The process **W1** → **W4** is endothermic by 29.9 kcal mol^{-1} with a substantial barrier of 33.4 kcal mol^{-1}. Note, however, that the latter reaction still has a lower barrier and is less endothermic than the [3+2] addi-
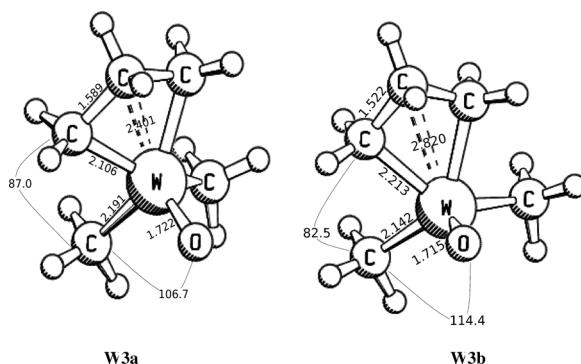

Fig. 3. Optimized structures at B3LYP/I of the isomeric forms **W3a** and **W3b** with selected interatomic distances in Å and angles in degree.

tion. Finally, the reaction of **W1** with C$_2$H$_4$ yielding **W5** can be regarded as a simultaneous [2+1] cycloaddition/elimination. The latter reaction gives cyclopropane and WO(CH$_3$)$_2$ as products. The process is endothermic by 30.3 kcal mol^{-1} with a barrier of 56.8 kcal mol^{-1}. The calculations predict that the [2+2]$_{W,C}$ addition of ethylene to **W1** is the kinetically and thermodynamically most favorable reaction, while the [3+2] addition is clearly less favored.

Fig. 3 shows the geometries of the energetically lowest lying reaction products **W3a** and **W3b** which are predicted to be formed *via* [2+2] addition of ethylene across the W=CH$_2$ bond. Isomer **W3a** has a significantly shorter distance between tungsten and the

Structure	WO(CH$_3$)$_2$(CH$_2$) (W1)		ReO$_2$(CH$_3$)(CH$_2$) (Re1)[a]		OsO$_3$(CH$_2$) (Os1)[b]	
	ΔE_R	ΔE_A	ΔE_R	ΔE_A	ΔE_R	ΔE_A
M1a	63.9	80.1	34.9	68.4	−27.5	41.3
M1b	4.5	49.8	−5.2	83.0	–	–
M1c	29.4	41.6	18.0[c]	30.3[c]	–	–
M1d	26.4	62.4	26.7	66.9	–	–
M1e	22.3	56.8	22.9[c]	60.9[c]	5.7[c]	57.1[c]

Table 1. Calculated reaction energies (ΔE_R) and activation energies (ΔE_A) for the isomerizations of WO(CH$_3$)$_2$(CH$_2$) (**W1**) in comparison with the corresponding rhenium and osmium systems **Re1** and **Os1** at B3LYP/II//B3LYP/I+ZPE. All values in kcal mol^{-1}.

Structure (cycloaddition)	W1 + C$_2$H$_4$		Re1 + C$_2$H$_4$ [a]		Os1 + C$_2$H$_4$ [b]	
	ΔE_R	ΔE_A	ΔE_R	ΔE_A	ΔE_R	ΔE_A
M2 ([3+2]$_{C,O}$)	37.0	52.5	6.7	35.7	−49.3	4.7
M3a ([2+2]$_{M,C}$)	−1.1	9.5	22.4	27.7	6.9	22.3
M3b ([2+2]$'_{M,C}$)	−1.9	1.6	−6.8	48.9	−10.9	37.7
M4 ([2+2]$_{M,O}$)	29.9	33.4	16.3	44.0	9.6	36.2
M5 ([2+1]$_{M,C}$)	30.3	56.8	25.3[c]	40.1[c]	−23.2[c]	–
M6	15.6	46.6	15.4[c]	42.6[c]	–	–
M7	38.5	78.4	9.2[c]	66.1[c]	−34.2	25.0
M8	10.6	39.5	10.8	36.3	−7.1	19.6

Table 2. Calculated reaction energies (ΔE_R) and activation energies (ΔE_A) for the addition of ethylene to WO(CH$_3$)$_2$(CH$_2$) (**W1**) in comparison with the corresponding rhenium and osmium systems **Re1** and **Os1** at B3LYP/II//B3LYP/I+ZPE. All values in kcal mol^{-1}.

[a] Taken from ref. [7]; [b] taken from ref. [6]; [c] these values of the osmium and rhenium systems were not published in ref. [6] and [7]; they are from more recent calculations by us.

C$_\beta$ atom of the ring (2.401 Å) than **W3b** which indicates stabilizing transannular interactions in the former species. Isomer **W3b** has a longer W–C$_\beta$ distance (2.820 Å) than **W3a** but the C–C bonds in the former species (1.522 Å) are much shorter than in **W3a** (1.589 Å).

Finally, there are three reaction pathways where the ethylene molecule adds to the oxygen atom of **1** with concomitant hydrogen migration. In the reaction **W1 → W7** a H atom migrates from ethylene to the methylene group of **W1** while in the reaction **W1 → W8** a hydrogen atom is transferred in the opposite direction. The latter reaction has a much lower activation barrier (39.5 kcal mol^{-1}) than the former process (78.4 kcal mol^{-1}). The reaction **W1 → W8** is also less endothermic (10.6 kcal mol^{-1}) than the reaction **W1 → W7** (38.5 kcal mol^{-1}). The ethylene addition to oxygen centers with simultaneous hydrogen atom transfer from a methyl group of **W1** to ethylene yielding **W6** is an endothermic reaction by 15.6 kcal mol^{-1} with a barrier of 46.6 kcal mol^{-1}. None of the latter three reactions should be able to compete with the ethylene [2+2] addition across the W=CH$_2$ bond.

Comparison with the ethylene addition to OsO$_3$(CH$_2$) and ReO$_2$(CH$_3$)(CH$_2$)

In the following, we compare the calculated activation barriers and reaction energies of the rearrangements shown in Fig. 1 and the ethylene addition reactions given in Fig. 2 for WO(CH$_3$)$_2$(CH$_2$) with the theoretical data which have been previously reported by us for the related molecules OsO$_3$(CH$_2$) [6] and ReO$_2$(CH$_3$)(CH$_2$) [7]. Table 1 shows the reaction energies and activation energies for the isomerization processes of the tungsten system **W1** and its corresponding rhenium (**Re1**) and osmium (**Os1**) analogs.

The energies for the C-O cyclization reaction yielding the metallaoxetanes **M1a** are very different for the tungsten, rhenium, and osmium systems. The reaction **M1 → M1a** which is strongly endothermic for $M =$ W becomes less endothermic for $M =$ Re and is even exothermic for $M =$ Os. The activation barriers decrease in the same order W > Re > Os but the activation barrier for the exothermic formation of the osmium isomer **Os1a** is still rather high (41.3 kcal mol^{-1}). The reaction **M1 → M1b** which is only available for $M =$ W, Re becomes slightly exothermic for the rhenium system but the activation barrier for the latter is much higher than for the tungsten compound. The very high barrier suggests that the rearrangement **Re1 → Re1b** is symmetry forbidden.

The methyl migration reaction **M1 → M1c** becomes somewhat less endothermic and has a lower activation barrier when $M =$ W than for $M =$ Re. The hydrogen migration from the methyl group to the oxo function **M1 → M1d** has very high activation barriers and similar reaction energies for tungsten and rhenium. The same situation is predicted by the calculated values for the hydrogen migration from the methylene group to oxygen **M1 → M1e** where the formation of the osmium isomer is only slightly endothermic but still has a high activation barrier.

Table 2 shows the reaction energies and reaction barriers for the addition of ethylene to **W1** and its corresponding rhenium and osmium analogs.

The [3+2]$_{C,O}$ cycloaddition yielding **W2** is endothermic, the reaction is nearly thermoneutral for **Re2** while it becomes strongly exothermic for **Os1**. We want to point out that the [3+2]$_{C,O}$ reaction **Os1** + C$_2$H$_4$ → **Os2** is clearly the most favorable process for the osmium system, both kinetically and thermodynamically. This is *not* the case for the tungsten and rhenium systems **W1** and **Re1**! The most favorable reactions of ethylene with **W1** and **Re1** are the [2+2]$_{M,C}$ cycloadditions across the *M*=C double bonds. The latter reaction shows some peculiar features which deserve to be discussed in more detail.

As shown above, the [2+2]$_{M,C}$ reaction of the tungsten system yielding first **W3a** which rearranges to the more stable isomer **W3b** is slightly exothermic by −3.0 kcal mol^{-1} and has an overall reaction barrier of only 9.5 kcal mol^{-1}. The pathways for the [2+2]$_{M,C}$ addition of the rhenium and osmium systems are qualitatively different from those of the tungsten compound. Unlike the tungsten system, the two isomeric forms **M3a** and **M3b** (*M* = Re, Os) come from two separate reaction channels of the [2+2]$_{M,C}$ addition **M1** + ethylene. We located two transition states for the reactions **M1** + ethylene → **M3a** and **M1** + ethylene → **M3b** for *M* = Re and Os while for *M* = W we could not find such a transition state. IRC calculations have clearly shown that the two transition states are connected to the different isomers **M3a** and **M3b** (*M* = Re, Os) [6, 7]. The latter [2+2]$_{M,C}$ additions yielding the isomers **M3b** are exothermic while the formation of **M3a** is endothermic (Table 2). Surprisingly, the exothermic reaction **M1** + ethylene → **M3b** has a higher barrier than the endothermic reaction **M1** + ethylene → **M3a**! This is an unusual finding which suggests that the former reaction is symmetry forbidden while the latter is not. There is no transition state for the interconversion between **Re3a** and **Re3b**. This is because the transition state for the reaction **Re1** + ethylene → **Re3a** is only 5.3 kcal mol^{-1} higher in energy than **Re3a**. A small geometrical distortion of the latter easily opens the channel for separation of ethylene. Searching for a transition state of interconversion between **Os3a** and **Os3b** was also not successful so far.

The [2+2]$_{M,O}$ addition of ethylene across the *M*=O bond, **M1** + ethylene → **M4**, is endothermic and it has high activation barriers for all metals *M* = W, Re, Os. It should not play a role in experimental studies. The [2+1] addition of ethylene to **M1** yielding cyclopropane and the metal fragment **M5** is also endothermic and has high activation barriers for *M* = W, Re, but for *M* = Os the reaction **Os1** + ethylene → cyclopropane + **Os5** becomes clearly exothermic by −23.2 kcal mol^{-1} (Table 2). We could not find a transition state for the latter process. However, in recent calculations we did find a transition state for the process **Os3b** → cyclopropane + **Os5**; the activation barrier of 31.0 kcal mol^{-1} is quite high.

The ethylene addition reactions to an oxygen atom of **M1** with concomitant hydrogen migration yielding **M6** – **M8** are endothermic and have high activation energies for *M* = W, Re. The reactions of the osmium system yielding **Os7** and **Os8** are exothermic and have medium activation energies which are clearly higher than for the [3+2] addition.

Summary

The calculations of the ethylene addition to **W1** predict that the energetically most favorable reaction is the [2+2]$_{W,C}$ addition across the W=C double bond yielding the metallacyclobutane **W3a** which then rearranges to the slightly more stable isomer **W3b**. The reaction is weakly exothermic by −3.0 kcal mol^{-1} and has an overall activation barrier of 9.5 kcal mol^{-1}. The [3+2]$_{C,O}$ addition of ethylene to **W1** is endothermic by 37.0 kcal mol^{-1} and has a very high barrier of 52.5 kcal mol^{-1}. All other addition reactions of C$_2$H$_4$ to **W1** are predicted to be endothermic and to possess high activation barriers and therefore, they should not play a role. Comparison with the rhenium and osmium systems shows significant differences particularly for **Os1**. The [3+2]$_{C,O}$ addition **Os1** + C$_2$H$_4$ → **Os2** is the thermodynamically most favorable reaction of the osmium compound which should proceed with a low activation barrier of only 4.7 kcal mol^{-1}. Unlike for the tungsten system, the reaction of the osmium compound is exothermic by −49.3 kcal mol. A possibly competing process for the latter is the cyclopropanation reaction for which the transition state could not be located. The reaction is exothermic by −23.2 kcal mol^{-1}. The [2+2]$_{M,C}$ addition of ethylene across the *M*=C double bond of **Os1** and **Re1** proceeds with two different pathways yielding the isomeric metallacycobutanes **M3a** and **M3b**. The formation of **M3b** is slightly exothermic for both metals but has higher activation energies than the [2+2]$_{M,C}$ addition yielding the less stable isomers **M3a**. For the rhenium system the [2+2]$_{Re,C}$ reactions are kinetically and thermodynamically more favorable

than the $[3+2]_{C,O}$ addition reaction which is slightly endothermic but has a rather high activation barrier of 35.7 kcal mol^{-1}. The ethylene addition reactions to the oxygen atom of **M1** with concomitant hydrogen migration yielding **M6** – **M8** are energetically unfavorable for M = W, Re. The latter reactions of the osmium system yielding **Os7** and **Os8** are exothermic, but the activation barriers are clearly higher than for the $[3+2]_{C,O}$ addition.

We want to emphasize that the results which are presented here do not answer all questions about the addition reaction of ethylene to the transition metal oxo compounds **M1**. For example, the question why the $[3+2]_{C,O}$ addition of ethylene to **Os1**, which is clearly favored over the $[2+2]_{M,C}$ addition, is strongly exothermic and has a low activation barrier while the same reaction of **W1** and **Re1** shows the opposite trend needs to be addressed. Other questions concern the rearrangement reactions which may take place in the metal oxo compounds prior to ethylene addition [6, 7]. We realize that this topic will require more work before definite conclusions can be drawn. The results which are presented here show that the investigation of the addition reaction of ethylene (and other unsaturated systems) deserves attention by computational chemistry. We continue with our efforts in the field.

Acknowledgement

[1] a) U. Pidun, C. Boehme, G. Frenking, *Angew. Chem.* **1996**, *108*, 3008; *Angew. Chem. Int. Ed.* **1996**, *35*, 2817; b) S. Dapprich, G. Ujaque, F. Maseras, A. Lledós, D. G. Musaev, K. Morokuma, *J. Am. Chem. Soc.* **1996**, *118*, 11660; c) A. M. Torrent, L. Deng, M. Duran, M. Sola, T. Ziegler, *Organometallics* **1997**, *16*, 13; d) A. J. Del Monte, J. Haller, K. N. Houk, K. B. Sharpless, D. A. Singleton, T. Straßner, A. A. Thomas, *J. Am. Chem. Soc.* **1997**, *119*, 9907.

[2] a) D. V. Deubel, G. Frenking, *J. Am. Chem. Soc.* **1991**, *121*, 2021; b) J. Frunzke, C. Loschen, G. Frenking. *J. Am. Chem. Soc.* **2004**, *126*, 3642; c) W.-P. Yip, W. Y. Yu, N. Zhu, C.-M. Che, *J. Am. Chem. Soc.* **2005**, *127*, 14239.

[3] Review: D. V. Deubel, G. Frenking, *Acc. Chem. Res.* **2003**, *36*, 645.

[4] D. V. Deubel, K. Muñiz, *Chem. Eur. J.* **2004**, *10*, 2475.

[5] M. Hölscher, W. Leitner, M. C. Holthausen, G. Frenking, *Chem. Eur. J.* **2005**, *11*, 4700.

[6] D. Cappel, S. Tüllmann, C. Loschen, M. C. Holthausen, G. Frenking, *J. Organomet. Chem.* **2006**, *691*, 4467. Note that the theoretical level of the calculations is slightly different from that in reference 7 and from that in the present work. Also, the transition states for the reactions **Os1** + ethylene → **Os3a** and **Os1** + ethylene → **Os3b** were only found after publication of this work. They are reported in reference 7.

[7] R. Haunschild, C. Loschen, S. Tüllmann, D. Cappel, M. Hölscher, M. C. Holthausen, G. Frenking, *J. Phys. Org. Chem.* in print.

[8] R. R. Schrock, *Chem. Rev.* **2002**, *102*, 145.

[9] T. Chen, Z. Wu, L. Li, K. R. Sorasaenee, J. B. Diminnie, H. Pan, I. A. Guzei, A. L. Rheingold, Z. Xue, *J. Am. Chem. Soc.* **1998**, *120*, 13519.

[10] a) A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648; b) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[11] P. J. Stevens, F. J. Devlin, G. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.

[12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, GAUSSIAN 03, Gaussian, Inc., Wallingford, CT (USA) **2004**.

[13] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829.

[14] D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, *Theor. Chim. Acta* **1990**, *77*, 123.

[15] a) K. Fukui, *J. Phys. Chem.* **1970**, *74*, 4161; b) K. Fukui, *Acc. Chem. Res.* **1981**, *14*, 363.

[16] J. M. L. Martin, A. J. Sundermann, *J. Chem. Phys.* **2001**, *114*, 3408.

[17] T. H. Dunning, *J. Chem. Phys.* **1989**, *90*, 1007.