Journal of Organometallic Chemistry 694 (2009) 1081–1090

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Ethylene addition to $Ru(=CH_2)(=O)_3$ – A theoretical study

Robin Haunschild [a], Sandor Tüllmann [b], Gernot Frenking [a,*], Max C. Holthausen [b,*]

[a] Fachbereich Chemie der Philipps-Universität Marburg, Hans-Meerwein-Straße, 35043 Marburg, Germany
[b] Institut für Anorganische Chemie der Johann Wolfgang Goethe-Universität, Max-von-Laue-Straße 7, D-60438 Frankfurt am Main, Germany

ARTICLE INFO

Article history:
Received 23 July 2008
Received in revised form 8 October 2008
Accepted 10 October 2008
Available online 17 October 2008

Keywords:
Oxidation reactions
Reaction mechanisms
Quantum chemical calculations
Ruthenium compounds
Carbenes

ABSTRACT

Quantum chemical calculations using density functional theory (B3LYP) were carried out to elucidate the reaction pathways for ethylene addition to the ruthenium compound RuO_3CH_2. These investigations show that the parent compound is relatively unstable and its rearrangement gives access to very diverse isomers and addition products with comparable relative energies and reaction barriers. The results are compared to our previous study on the analogous osmium system OsO_3CH_2 and we show that reactivity of both compounds towards ethylene is quite similar. In both cases, the $[3+2]_{C,O}$ cycloaddition pathway is preferred kinetically and thermodynamically. The exothermicity (−68.8 kcal/mol) of this reaction is higher for the ruthenium system than for the osmium homologue. While this pathway is unrivaled for the osmium system, the $[3+2]_{O,O}$ cycloaddition pathway is able to compete kinetically for the ruthenium system.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The use of OsO_4 as catalyst for *cis*-dihydroxylation of olefins has become a standard procedure in organic chemistry [1]. After some debate about the nature of the initial addition step, quantum chemical studies clearly revealed that it is a concerted [3 + 2] addition process yielding an osma-2,5-dioxolane. The alternatively suggested route (i.e., [2 + 2] addition followed by subsequent rearrangement of the osmaoxetane) was shown to have much higher activation barriers [2]. For RuO_4, a similar reaction mechanism was proposed [3] and the [3 + 2] initial step is supported by recent experiments [4]. While these findings are now undisputed in the community, much less is known about the reactivity of ethylene with transition metal compounds containing doubly bonded ligands (=X) other than oxygen. In this context we note that Deubel and Muñiz reported a theoretical study of the ethylene addition to $OsO_2(NH)_2$ and clearly showed that again [3 + 2] addition dominates over [2 + 2] addition pathways [5].

However, a considerably different picture arose in our recent theoretical studies on the corresponding reactivity of the related carbene species $OsO_3(CH_2)$ [6], $OsO_2(CH_2)_2$ [7], $ReO_2(CH_2)(CH_3)$ [8], as well as $WO(CH_2)(CH_3)_2$ [9], and the other group-6 analogs [10] with ethylene. For some of these systems, the [2 + 2] addition of ethylene becomes competitive or even more favorable than the [3 + 2] addition reaction. Further, compared to the binary metal oxides, substantially more complicated reaction profiles were identified in these studies, because C–C and C–O ring closure reactions can lead to a number of thermodynamically favorable intermediates that open up further reaction pathways. Interestingly, Schrock has recently reported the synthesis of $RR'W(NAr)(CHCMe_3)$ and its reaction with ethylene yielding $RR'W(NAr)(CH_2)$ and $H_2C{=}CHCMe_3$, which indicates that a [2 + 2] addition across the $W{=}CHCMe_3$ double bond has taken place [11].

As part of our ongoing studies of ethylene addition to such species we present here results of quantum chemical calculations on the ethylene addition to $RuO_3(CH_2)$, the Ru homologue of $OsO_3(CH_2)$ studied earlier [8]. A comparison of the reaction pathways identified for these two systems is made in order to illustrate similarities and differences caused by variation of the transition metal ion within an identical ligand environment.

2. Computational details

All calculations have been performed at the density functional theory (DFT) level employing the B3LYP hybrid functional [12] as implemented [13] in the GAUSSIAN03 program [14]. The TZVP all electron basis set of Ahlrichs and coworkers was employed for C, O, and H [15]. For Ru the Stuttgart/Köln relativistic effective core potentials replacing 28 core electrons were used in combination with (311111/22111/411) valence basis sets [16]. This combination is denoted here as basis set I. All minima and transition structures were optimized at this level of theory without symmetry constraints. Analytic Hessians computed at B3LYP/I were used to characterize the nature of stationary points as local minima or transition states and to obtain (unscaled) zero-point vibrational energy contributions (ZPE). All connectivities of minima and

---

* Corresponding authors.
E-mail addresses: Frenking@chemie.uni-marburg.de (G. Frenking), Max.Holthausen@chemie.uni-frankfurt.de (M.C. Holthausen).

0022-328X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2008.10.017

transition structures were verified by either intrinsic reaction coordinate (IRC) [17] or dynamic reaction path (DRP) [18] following calculations with a slightly different valence basis set for Ru. Here, the triple-ζ quality valence basis set (31111/411/311) was used [19]. Based on the B3LYP/I geometries additional single point calculations were performed employing the larger basis set II, in which the Stuttgart/Köln valence basis set for Ru was augmented by two sets of *f*-functions and one set of *g*-functions derived by Martin and Sundermann [20] and used in combination with the correlation consistent cc-pVTZ basis set of Dunning [21] for C, O, and H atoms. All relative energies discussed below relate to B3LYP/II/B3LYP/I calculations and include ZPE contributions. While the B3LYP functional used together with basis sets of triple-ζ quality can show errors in computed barrier heights as large as 4–7 kcal/mol [22] we found by comparison to CCSD(T)/II calibration data in earlier work [7] relative energies obtained at the B3LYP/II//B3LYP/I level superior to relative energies directly obtained from B3LYP/I calculations. Our present results are consistent and directly comparable with our previously published data in [6], but please note that a different basis set was used in our first report [8] on the reactivity of $OsO_3(CH_2)$ against ethylene.

3. Results and discussion

The focus of this work lies on the calculated reaction profiles for the addition of ethylene to RuO_3CH_2 ($^{\mathbf{Ru}}\mathbf{1}$) and the comparison to those predicted earlier for OsO_3CH_2 ($^{\mathbf{Os}}\mathbf{1}$). We refrain from a detailed discussion of molecular structures, but a complete set of coordinates and total energies (B3LYP/I and B3LYP/II//B3LYP/I) of all ruthenium species discussed is given as Supporting Information.

In our previous studies on ethylene addition to alkylidene species $L_nM(CH_2)(O)$, we found that the parent complex may rearrange to more stable isomers [6–9]. We thus commenced our study with a search for conceivable isomers of RuO_3CH_2 (**1**) and the associated transition structures. The results are shown in Fig. 1.

Indeed, we found that, with the two exceptions **1c** and **1e** (26.6 and 31.3 kcal/mol relative to **1**, respectively), all identified isomers are more stable than **1**. Notably, the ruthenaoxirane isomer **1a** is substantially more stable than **1** by 51.2 kcal/mol. The O–C coupling step proceeds via **TS1→1a** and is connected with a barrier of 28.6 kcal/mol. The resulting species can then rearrange to **1d** which can be interpreted as the end-on complex of formaldehyde and RuO_2. The barrier involved in this process is moderate

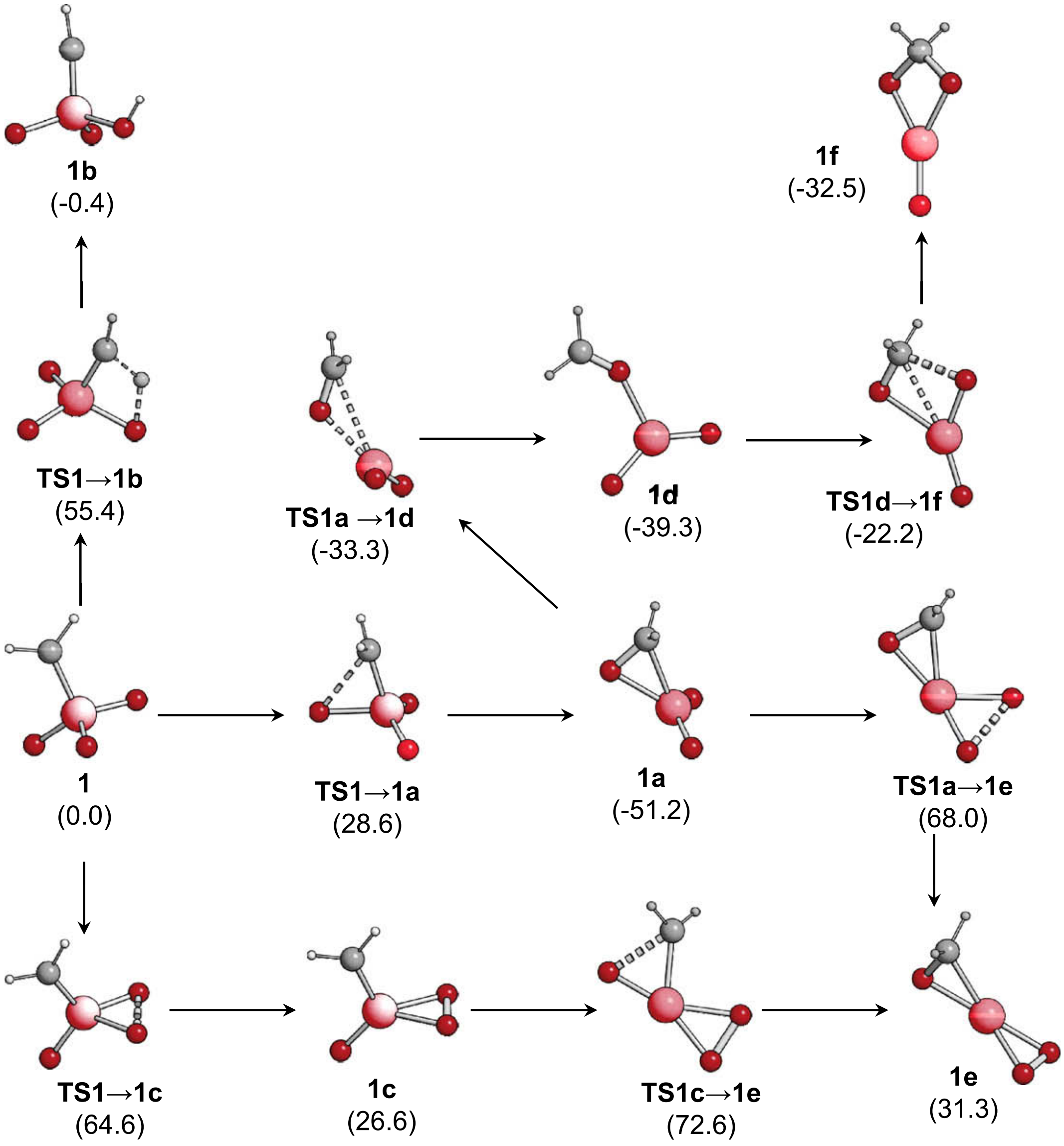

Fig. 1. Isomerization pathways of **1** (energies in kcal/mol relative to **1** + C_2H_4).

Download English Version:

https://daneshyari.com/en/article/1324657

Download Persian Version:

https://daneshyari.com/article/1324657

Daneshyari.com