J|A|C|S
COMMUNICATIONS

Published on Web 05/24/2007

Computational Insights into Degenerate Ethylene Exchange with a Grubbs-Type Catalyst

Charles Edwin Webster

Department of Chemistry, 213 Smith Chemistry Building, The University of Memphis, Memphis, Tennessee 38152-3550

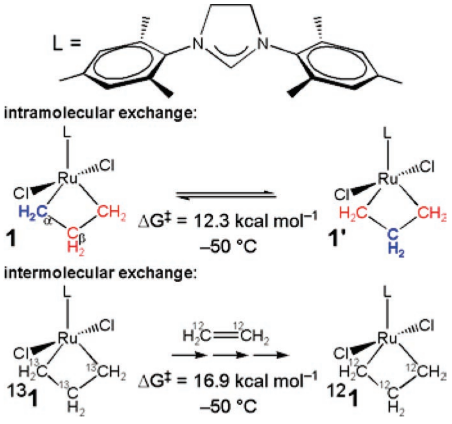
Received March 6, 2007; E-mail: charles.webster@memphis.edu

Olefin metathesis reactions, which exchange the substituents about the double bonds of the alkenes, are important for a variety of chemical syntheses.[1] Specific transition metal-containing catalysts perform olefin metathesis reactions and find wide use because the carbon−carbon double bond, which is rather unreactive, can be activated under mild conditions, even in aqueous media.[2] The mechanism and postulated intermediates of the metathesis reaction have been the subject of numerous experimental[3] and theoretical[4] studies. A metallocyclobutane intermediate has been implicated in the mechanism of the Grubbs-type catalyzed olefin metathesis. Romero and Piers recently reported an experimental mechanistic study[3a] of ethylene exchange with a 14-electron ruthenacyclobutane, $(NHC)Cl_2Ru(CH_2CH_2CH_2)$, where NHC is an N-heterocyclic carbene (1,3-dimesitylimidazolidin-2-ylidene), derived from a second generation Grubbs catalyst, see Scheme 1. They described (1) intramolecular exchange of C_α and C_β in **1** and (2) intermolecular exchange, the degenerate exchange of free ethylene with **1**. Each exchange mechanism could have paths with cis or trans chlorides.[5] The activation parameters for the ethylene exchange process were determined to be $\Delta H^\ddagger = 13.2(5)$ kcal mol^{-1} and $\Delta S^\ddagger = -15(2)$ eu. Romero and Piers called for "further investigations, particularly computational studies" on their mechanistic proposals. In this Communication, density functional theory calculations[6] are applied to test these proposed mechanisms and consider dissociative versus associative mechanisms at elevated temperatures at which these olefin metathesis catalysts are also used.

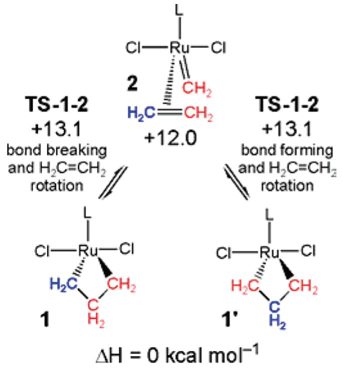
For intramolecular carbon exchange, one could envision a two-step mechanism that would in the first step cleave the metallocyclobutane and in the second step rotate the coordinated ethylene. Alternatively, our computational results indicate a single-step mechanism starting from the ruthenacyclobutane complex (**1**) directly producing the ethylene ruthenium carbene complex (**2**) by a rotational bond-breaking transition state (**TS-1−2**, see Scheme 2). **2** has a coordinated ethylene which is essentially perpendicular to the remaining methylene unit. This result is in agreement with the previously reported computational work of Adlhart and Chen.[4e] That is, in **2**, ethylene is aligned parallel to the Cl−Ru−Cl vector, and no minimum energy structure with ethylene perpendicular to the Cl−Ru−Cl vector could be located; this structure simply optimizes to **1**.[7] In **2** ethylene is essentially trans to L and the methylene CH_2 plane is perpendicular to the L-Ru-centroid$_{(CH_2{=}CH_2)}$ vector; no minimum energy structure with methylene trans to L could be located. The structures of **1** and **2** have trans-disposed chlorides; the cis-disposed chloride analogues of **1** and **2** are higher in energy than the trans-disposed chlorides by 11.2 and 13.3 kcal mol^{-1}, respectively (see Supporting Information).

For intermolecular ethylene exchange, one could envision a variety of mechanisms. Ethylene could bind to **1** or **2** and a postulated metallocylohexane transition state or intermediate could be involved in the exchange. These structures could have either trans-disposed or cis-disposed chloride analogues. Our computational results indicate a multistep mechanism with structures that have trans-disposed, not cis-disposed chlorides (see Figure 1 and the Supporting Information). Starting from **3** (ethylene associated with **1**), ethylene binds (through **TS-3−5**), which produces the η^2-ethylene ruthenacyclobutane complex (**5**). A rotational bond-breaking transition state (**TS-5−6**) produces **6** (a bis ethylene methylene complex),[8] from which the ethylene trans to NHC can dissociate (through **TS-4−6**). A second ruthenacyclobutane complex with associated ethylene (**9**) is formed through **TS-4−9** (similar to **TS-1−2**). From **5**, η^2-ethylene rotates (through **TS-5−7**) to form **7**. A ruthenacyclohexane intermediate (**8**) that is higher in energy is formed through **TS-7−8**. While the proposed pathway is not an energetically symmetric pathway, it does not violate the principle of microscopic reversibility (PMR).[9,10]

Scheme 1. Experimental Observations by Romero and Piers



Scheme 2. Calculated Enthalpies of Optimized Structures for the Lowest-Energy Proposed Mechanism for Intramolecular Carbon Exchange



For the intramolecular mechanisms (without a second-coordinated ethylene) that simply exchange C_α and C_β of the ruthenacyclobutane, one may conclude from our computational results that (1) they are lower in energy than the mechanisms with a second-

10.1021/ja071588d CCC: $37.00 © 2007 American Chemical Society

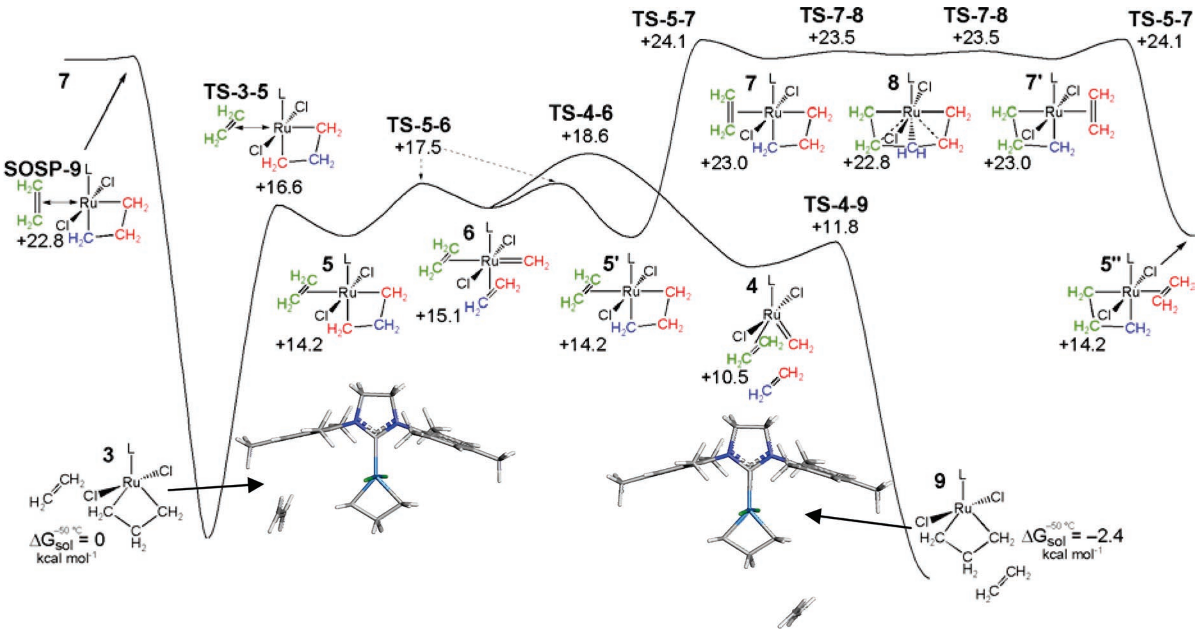


Figure 1. Relative free energies ($\Delta G^{\ddagger,-50°C}_{CH_2Cl_2}$) for the intermolecular exchange of ethylene.

coordinated ethylene (consistent with experimental results); (2) the structures with trans-disposed chlorides are lower in energy than ones with cis-disposed chlorides; (3) the pathway with trans-disposed chlorides has a lower barrier than the pathway with cis chlorides; and (4) the computed free energy of activation including solvation for the pathway with trans-disposed chlorides ($\Delta G^{\ddagger,-50°C}_{CH_2Cl_2}$ $= 14.4$ kcal mol^{-1}) is close to the observed free energy of activation ($\Delta G^{\ddagger,-50°C}_{CD_2Cl_2} = 12.3$ kcal mol^{-1}).

For the intermolecular mechanisms (with a second-coordinated ethylene) that exchange ethylenes, one may conclude from our computational results that (1) the structures with trans-disposed chlorides are lower in energy than ones with cis-disposed chlorides; (2) the pathway with trans-disposed chlorides has a lower barrier than the pathways with cis chlorides; (3) the lowest energy pathway does not include a ruthenacyclohexane intermediate or transition state structure; (4) the computed free energy of activation including solvation ($\Delta G^{\ddagger,-50°C}_{CH_2Cl_2} = 18.6$ kcal mol^{-1}) is close to the experimentally measured value ($\Delta G^{\ddagger,-50°C}_{CD_2Cl_2} = 16.9$ kcal mol^{-1}); (5) an estimated barrier (with a speculative solvent correction) for the pathway with trans-disposed chlorides ($\Delta H^{\ddagger} = 17.6$ kcal mol^{-1}) is comparable to the observed barrier ($\Delta H^{\ddagger} = 13.2(5)$ kcal mol^{-1}); and (6) the computed entropy of activation (−7.3 eu) is consistent with an associative mechanism and somewhat similar to the measured value (−15(2) eu).

Romero and Piers suggested that a competing mechanism involving dissociation of ethylene from **1** at elevated temperatures could become competitive with the associative mechanism. To test that suggestion, the relative free energy of ethylene loss from **1** was computed. A rise of the temperature to 100 °C (from −50 °C) increases the stability of separated ethylene and the methylene fragment by ~11.8 kcal mol^{-1} when compared to **3** (see Supporting Information). Therefore, ethylene dissociation from **1** could become the operative pathway at elevated temperatures.

Design and modification of catalyst ligands and catalysts is directly impacted by the understanding of the details of the mechanism of the catalyzed reaction. This current computational study provides support for a single-step intramolecular mechanism for the exchange of adjacent methylene groups and an associative multistep intermolecular mechanism for the exchange of ethylene that does not involve a metallocyclohexane intermediate or transition state.

Acknowledgment. The author thanks Professors Michael B. Hall and Warren E. Piers for invaluable comments and the Department of Chemistry at the University of Memphis for supporting this work.

Supporting Information Available: Complete ref 6, computational details, further details, and geometric details. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Grubbs, R. H., Ed. *Handbook of Metathesis*; Wiley-VCH: New York, 2003.
(2) (a) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18−29. (b) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592−4633. (c) Schrock, R. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 3748−3759. (d) Grubbs, R. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 3760−3765.
(3) (a) Romero, P. E.; Piers, W. E. *J. Am. Chem. Soc.* **2007**, *129*, 1698−1704. (b) Anderson, D. R.; Hickstein, D. D.; O'Leary, D. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 8386−8387. (c) Romero, P. E.; Piers, W. E. *J. Am. Chem. Soc.* **2005**, *127*, 5032−5033.
(4) (a) Aagaard, O. M.; Meier, R. J.; Buda, F. *J. Am. Chem. Soc.* **1998**, *120*, 7174−7182. (b) Cavallo, L. *J. Am. Chem. Soc.* **2002**, *124*, 8965−8973. (c) Vyboishchikov, S. F.; Buhl, M.; Thiel, W. *Chem.—Eur. J.* **2002**, *8*, 3962−3975. (d) Fomine, S.; Vargas, S. M.; Tlenkopatchev, M. A. *Organometallics* **2003**, *22*, 93−99. (e) Adlhart, C.; Chen, P. *J. Am. Chem. Soc.* **2004**, *126*, 3496−3510. (f) Suresh, C. H.; Koga, N. *Organometallics* **2004**, *23*, 76−80. (g) Straub, B. F. *Angew. Chem., Int. Ed.* **2005**, *44*, 5974−5978. (h) Suresh, C. H.; Baik, M.-H. *J. Chem. Soc., Dalton Trans.* **2005**, 2982−2984. (i) Benitez, D.; Goddard, W. A., III. *J. Am. Chem. Soc.* **2005**, *127*, 12218−12219. (j) Fomine, S.; Ortega, J. V.; Tlenkopatchev, M. A. *J. Mol. Catal. A: Chem.* **2005**, *236*, 156−161. (h) Correa, A.; Cavallo, L. *J. Am. Chem. Soc.* **2006**, *128*, 13352−13353. (i) Kuznetsov, V. F.; Abdur-Rashid, K.; Lough, A. J.; Gusev, D. G. *J. Am. Chem. Soc.* **2006**, *128*, 14388−14396. (j) Fomine, S.; Ortega, J. V.; Tlenkopatchev, M. A. *J. Organomet. Chem.* **2006**, *691*, 3343−3348. (k) Occhipinti, G.; Bjorsvik, H.-R.; Jensen, V. R. *J. Am. Chem. Soc.* **2006**, *128*, 6952−6964.
(5) For the plausible mechanisms of exchange, see ref 3a.
(6) PBE DFT calculations with mixed DZP/DZ basis sets performed with the following: Frisch, M. J.; et al. *Gaussian 03*, revision C02; Wallingford, CT, 2004.
(7) One could constrain the $C_{CH2}-C_{CH2=CH2}$ distance and optimize to a geometry that represents this hypothetical structure. In this region, the PES is high in energy, but relatively flat (see Supporting Information).
(8) **TS-2−6** also produces **6** (see Supporting Information).
(9) PMR does not preclude an energetically unsymmetrical pathway (see Burwell, R. L.; Pearson, R. G. *J. Phys. Chem.* **1966**, *70*, 300−302).
(10) Yang, X.; Hall, M. B. *J. Am. Chem. Soc.* **2007**, *129*, 1560−1567 is a recent example of computational study of an associative ligand exchange mechanism that does not violate PMR.

JA071588D