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DFT Study of the Isomerization and Spectroscopic/Structural Properties of Ruthenacyclobutane Intermediates Relevant to Olefin Metathesis

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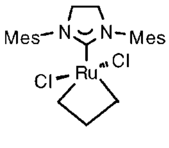
Summary: NMR chemical shifts and $^{1}J(C_{\alpha}C_{\beta})$ *constants of substituted and unsubstituted ruthenacyclobutanes were calculated using DFT and were found to be in good agreement with experiment. Notably, these calculations confirm that the difference between metallacycle* $^{1}J(C_{\alpha}C_{\beta})$ *constants correlate to* $C_{\alpha}-C_{\beta}$ *activation. The relative stabilities of the unimolecular ROM and RCM pathways are consistent with literature reports.*

Olefin metathesis has become a widely used technique in broad ranging fields of chemistry.[1] Ruthenium-based catalysts pioneered by Grubbs[2] have been notably successful for this purpose. The second-generation Grubbs catalyst,[3] which features a ruthenium alkylidene and a 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene N-heterocyclic carbene support ligand, is understood to effect metathesis through a [2 + 2] cycloaddition between the olefin and the metal-alkylidene bond to form a ruthenacyclobutane intermediate. Cycloreversion to form the opposing carbene generates the metathesis product.

Observation of the critical cycloaddition and cycloreversion steps of the catalytic cycle have been hindered by the tendency of the catalyst to retain the coordinated PR_3 ligand present in the parent complex. Recently, Piers et al. synthesized the ruthenacyclobutanes **1** and **2** through the reaction of a phosphonium alkylidene with ethylene[4] and dimethyl cyclopent-3-ene-1,1-dicarboxylate,[5] respectively. The direct observation of these stable ruthenacyclobutane metathesis intermediates has allowed some of the critical steps of metathesis to be studied directly.[6]



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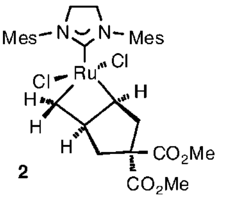

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On the basis of the NMR spectra, Romero and Piers concluded that **1** has C_{2v} symmetry with a kite-shaped metallacycle,[4] which was further supported by Wenzel and Grubbs,[4,7] although the spectra showed several unusual features. The

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(1) Grubbs, R. H., Ed. *Handbook of Metathesis*; Wiley-VCH: Weinheim, Germany, 2003.

(2) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.

(3) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953.

(4) Romero, P. E.; Piers, W. E. *J. Am. Chem. Soc.* **2005**, *127*, 5032.

(5) van der Eide, E. F.; Romero, P. E.; Piers, W. E. *J. Am. Chem. Soc.* **2008**, *130*, 4485.

(6) Romero, P. E.; Piers, W. E. *J. Am. Chem. Soc.* **2007**, *129*, 1698.

(7) Wenzel, A. G.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 16048.

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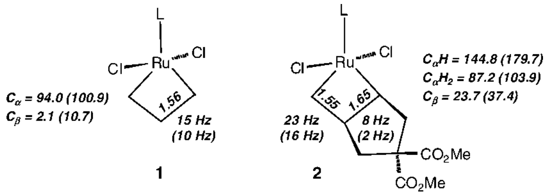

Figure 1. C_α and C_β chemical shifts (ppm) and $^1J(C_\alpha C_\beta)$ coupling constants (Hz). Calculated values are given in parentheses. Calculated $C_\alpha-C_\beta$ bond lengths (Å) are also shown.

metallacycle C_α resonance appears much further downfield than C_β, a characteristic typical of group IV[8] and VI[9] metallacyclobutanes and opposite to the case for platinum group metallacyclobutanes.[10] Further, $C_\alpha-C_\beta$ coupling constants in **1** (15 Hz) and **2** (23 and 8.5 Hz) are atypically small and point to activation of all of these C−C bonds. With regard to **2**, although both C−C bonds are activated, the 14 Hz difference in $^1J(C_\alpha(H)C_\beta)$ and $^1J(C_\alpha(H_2)C_\beta)$ suggest that the former is activated to a greater extent than the latter.[5] To provide support for the assigned structures of these crucial metathesis intermediates and better understand their reactivity, we have used density functional theory (DFT)[11,12] to calculate the metallacycle chemical shifts and $^1J(C_\alpha C_\beta)$ coupling constants, as well as the unimolecular metathesis pathways of **2**.

Consistent with the experimental reports, our calculated ^{13}C chemical shifts show high-field C_β and low-field C_α resonances, as well as reasonable absolute agreement with the experimental data (Figure 1). $C_\alpha-C_\beta$ coupling constants are also in acceptable agreement, with small (2−16 Hz) values calculated for **1** and **2**. The calculated values are in very good agreement with the 14 Hz difference in the $C_\alpha-C_\beta$ coupling constants of **2**, where $^1J(C_\alpha H_2-C_\beta)$ is 23 Hz but $^1J(C_\alpha(H)C_\beta)$ is 8.5 Hz.[13] These results provide strong support for the ruthenacyclobutane structures assigned by Piers et al.[4,5]

The origin of the large difference in $C_\alpha-C_\beta$ coupling constants in **2** is apparent in its DFT optimized structure; the substituted $C_\alpha H-C_\beta$ bond is elongated to 1.65 Å, while the $C_\alpha H_2-C_\beta$ bond has a more typical C−C bond length of 1.55 Å. Remarkably, the modest 6.2 kcal mol^{-1} ring strain present in the cyclopentane ring[14] is sufficient to induce this 0.1 Å increase in the metallacycle bond length.[15] Given this elongation, **2** provides an unprecedented insight into the mechanism of metathesis, as it is effectively arrested midway through cycloreversion.

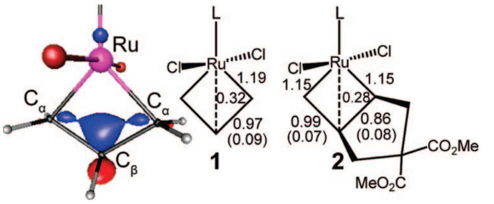

Figure 2. MO of **1** showing the $C_\alpha-C_\beta-$Ru interactions (left) and bond orders of **1** and **2**. (C−C)→Ru three-center bond orders are shown in parentheses.

Although the $C_\alpha H-C_\beta$ bond length in the minimum energy geometry of **2** is 1.65 Å, we calculated the difference in $C_\alpha C_\beta$ coupling constants when the $C_\alpha H-C_\beta$ bond length was constrained to a range of values from 1.56 Å to 1.7 Å in order to elaborate the effect of ruthenacyclobutane geometry on the $C_\alpha-C_\beta$ coupling constants. The $C_\alpha H-C_\beta$ coupling constant sharply declines as the distance increases and the $C_\alpha H_2 C_\beta$ coupling constant increases concomitantly. This difference in coupling constants correlates linearly to the elongation of the 1,2 substituted ruthenacyclobutane $C_\alpha H-C_\beta$ bond (Eqn 1).

$$r(C_\alpha H_2, C_\beta) = 0.0076\ \Delta^1 J(C_\alpha C_\beta) + 1.56 \qquad (1)$$

$(C_\alpha C_\beta)\rightarrow M$ agostic interactions have been proposed to be active in the stabilization of metallacyclobutanes[16] and to play a role in the stabilization of **1**.[17] Interestingly, Mayer bond order analysis[18] of **1** shows that the ruthenacyclobutane three-center−two-electron (3c2e) interactions between the $C_\alpha-C_\beta$ bonds and the metal are modest, with bond orders of 0.09, suggesting that the formally three-center component of the metal−propane-1,4-diyl interaction is not dominant (Figure 2, right). A stronger interaction is available through the direct two-center bonding between C_β and the metal, which has a bond order of 0.32. This is apparent in the molecular orbital corresponding to the metal−metallacycle agostic interactions, which is dominated by the covalent overlap of a C_β p orbital and the Ru d_{z^2} orbital (Figure 2, left), which accounts for the short 2.27 Å Ru−C_β distance and high-field C_β resonance. These interactions are somewhat weaker in **2**, where the 3c2e $C_\alpha H-C_\beta-$Ru and $C_\alpha H_2-C_\beta-$Ru interactions have bond orders of 0.047 and 0.051, respectively, and the Ru−C_β bond order is 0.28. The $C_\alpha-C_\beta$ bond orders of **2** are sharply different (0.99 for $C_\alpha H_2-C_\beta$ and 0.086 for $C_\alpha H-C_\beta$), reflecting their different activations. Although one would intuitively expect that the Ru−C_αH carbene and $C_\alpha H_2-C_\beta$ double-bond character in **2** to be larger than in **1**, **2** retains the ruthenacyclobutane bonding motif, with equal Ru−C_α bond orders despite the elongated $C_\alpha H-C_\beta$ bond. Double-bond and carbene formation do not occur until late in the cycloreversion.

Two important metathesis pathways available in **2** are ring-opening metathesis (ROM),[19] where a cyclic olefin is opened, and ring-closing metathesis (RCM),[20] where a cyclic olefin is formed from a diene; the former is a key step in ring-opening metathesis polymerization (ROMP). In the ROM pathway, **2** undergoes cycloreversion to form **3**, an alkylidene with a terminal alkene that coordinates to metal in the coordination site trans to the H_2IMes in an η^2 fashion (Figure 3). This

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(8) (a) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876. (b) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 7491.

(9) (a) Feldman, J.; Murdzek, J. S.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 2260. (b) Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R. *Organometallics* **1990**, *9*, 2535. (c) Tsang, W. C. P.; Jamieson, J. Y.; Aeilts, S. L.; Hultzsch, K. C.; Schrock, R. R.; Hoveyda, A. H. *Organometallics* **2004**, *23*, 1997.

(10) (a) Diversi, P.; Ingrosso, G.; Lucherini, A.; Marchetti, F.; Adovasio, V.; Nardelli, M. *J. Chem. Soc., Dalton Trans.* **1991**, 203. (b) McNeill, K.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 11244.

(11) NMR calculations used ADF 2005.1 with BP86/QZP. Mesityl groups were truncated to methyls and the methyl carboxylates in **2** were truncated to hydrogens. Bond order and reaction profile calculations used Turbomole with BP86/def2-SV(P), without truncation.

(12) Ziegler, T.; Autschbach, J. *Chem. Rev.* **2005**, *105*, 2695.

(13) We have also calculated the ruthenacycle $^1J(C_\alpha C_\beta)$ coupling constants and ^{13}C chemical shifts for alternative cis-chloride isomers of **1** and **2**, which are also in reasonable agreement with the experimental data; however, these configurations can be rejected on the basis of other criteria. See the Supporting Information for details.

(14) Kenneth, B. W. *Angew. Chem., Int. Ed.* **1986**, *25*, 312.

(15) Previous DFT studies observed this asymmetry in other substituted ruthenacyclobutanes. See: (a) Adlhart, C.; Chen, P. *J. Am. Chem. Soc.* **2004**, *126*, 3496. (b) Cavallo, L. *J. Am. Chem. Soc.* **2002**, *124*, 8965.

(16) Harvey, B. G.; Mayne, C. L.; Arif, A. M.; Ernst, R. D. *J. Am. Chem. Soc.* **2005**, *127*, 16426.

(17) (a) Suresh, C. H.; Koga, N. *Organometallics* **2004**, *23*, 76. (b) Suresh, C. H.; Baik, M.-H. *Dalton Trans.* **2005**, 2982.

(18) Gorelsky, S. I. AOMix: Program for Molecular Orbital Analysis; University of Ottawa, Ottawa, Ontario, Canada, 2007; http://www.sg-chem.net/.

(19) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2903.

(20) Conrad, J. C.; Fogg, D. E. *Curr. Org. Chem.* **2006**, *10*, 185.

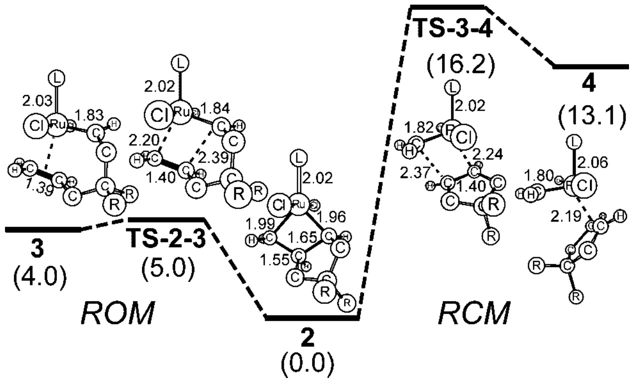
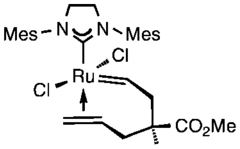


Figure 3. Reaction profile for ROM and RCM isomerizations of **2**. Distances (Å) are adjacent to select bonds. Energies (kcal mol^{-1}) are given in parentheses.



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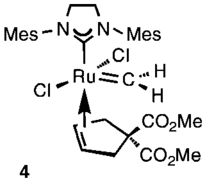

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pathway has a 5.0 kcal mol^{-1} barrier (**TS-2−3**) with **3** lying 4.0 kcal mol^{-1} higher in energy than **2**. Alternatively, **2** can go through the RCM pathway, forming **4**, where a dimethyl cyclopent-3-ene-1,1-dicarboxylate−ruthenium adduct is formed. **4** is a higher energy structure than **2** and **3**, with a relative energy of 13.1 kcal mol^{-1}. The RCM transition state structure (**TS-3−4**) has a barrier of 16.2 kcal mol^{-1}. The RCM pathway is higher in energy due to the greater ring strain in the cyclopentene formed through the ring closing and the greater stability of the Ru−alkylidene in **3** compared to the methylidene in **4**. This is consistent with the trapping and NMR exchange experiments of van der Eide et al.,[5] who tentatively concluded that **3** is more stable than **4**.

This reaction profile illustrates the remarkable metathesis abilities of the Grubbs catalyst. Cycloaddition to form the ruthenacyclobutane from either the ROM or RCM adducts occurs with very small barriers, as the olefin adducts can isomerize to the metallacycle through a continuous range of low-energy geometries. ($C_\alpha C_\beta$)→Ru agostic and Ru−C_β bonding are largely able to compensate for the energetic cost of breaking a C−C bond during the cycloreversion, allowing the metathesis process to proceed without crossing large energetic barriers.

In conclusion, we have found that the ^{13}C chemical shifts and $^1J(C_\alpha C_\beta)$ values calculated using DFT are consistent with the assigned structures of the unsubstituted (**1**) and substituted (**2**) ruthenacyclobutanes. The C_αH−C_β bond in **2** is elongated to 1.65 Å by the ring strain of the cyclopentane ring. A large difference in metallacyclobutane $^1J(C_\alpha C_\beta)$ constants indicates a strongly activated C_α−C_β bond. These metallacycles are stabilized by a covalent C_β−Ru interaction and, to a lesser degree, a 3c2e ($C_\alpha C_\beta$)→Ru interaction. **2** can facilely isomerize to a ROM related adduct (**3**) or to a RCM related adduct (**4**) through a higher energy path.

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Supporting Information Available: Text, figures, and tables giving details of the calculations, coupling constant data, and coordinates of species. This material is available free of charge via the Internet at http://pubs.acs.org.

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