

## Model Compounds of Ruthenium–Alkene Intermediates in Olefin Metathesis Reactions

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Received March 15, 2006; E-mail: rhg@caltech.edu

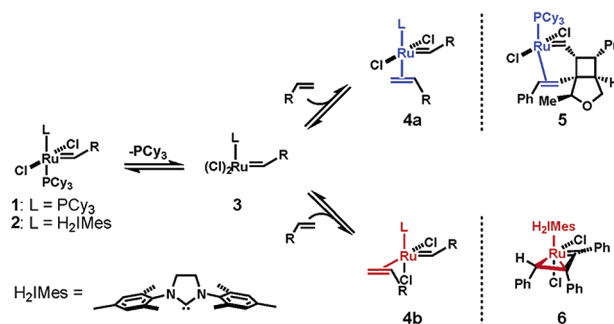
With the advent of well-defined and stable catalysts, olefin metathesis has become a versatile synthetic tool for carbon–carbon double bond construction.<sup>1</sup> Among reported olefin metathesis catalysts, **1**<sup>2</sup> and **2**<sup>3</sup> have received significant attention from and widespread use by synthetic chemists due to their activity, functional group tolerance, and commercial availability.<sup>4</sup>

The general mechanism for transition-metal-catalyzed olefin metathesis, as proposed by Chauvin and co-workers, involves olefin binding to a metal alkylidene species, metallacyclobutane formation, and subsequent generation of another olefin and metal alkylidene species.<sup>5</sup> Previous mechanistic studies of **1**<sup>6</sup> and **2**<sup>7</sup> in olefin metathesis reactions have focused on catalyst initiation and demonstrated that phosphine dissociates to generate coordinatively unsaturated ruthenium alkylidene species **3** which can then bind an olefin and enter the catalytic cycle (Scheme 1). These studies enabled the design and synthesis of catalysts with higher initiation rates for use in living polymerizations.<sup>8</sup> However, few experimental studies<sup>9</sup> have been performed to provide an understanding of olefin binding geometry and metallacyclobutane formation;<sup>10</sup> these steps in the catalytic cycle are essential to the rational design of diastereoselective and enantioselective<sup>11</sup> catalysts.

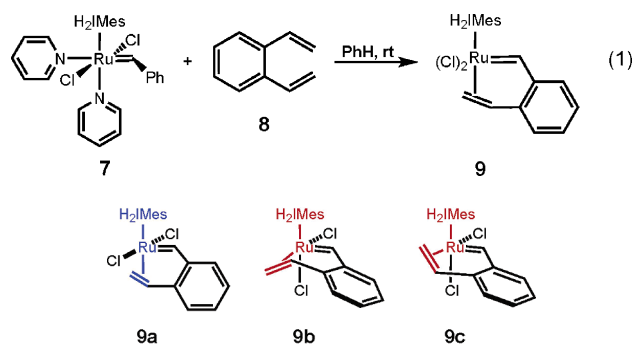
Postulated olefin binding scenarios include intermediate **3** either binding olefin preferentially trans (**4a**) or cis (**4b**) to the L-type ligand or binding olefin nonpreferentially through a mixture of intermediates **4a** and **4b** (Scheme 1). Snapper and co-workers isolated complex **5** in which a chelating olefin is tethered through the alkylidene and coordinates trans to the PCy<sub>3</sub> ligand (bottom-bound).<sup>12</sup> Additional evidence for a bottom-bound mechanism was provided by Piers and co-workers who observed a C<sub>2v</sub> symmetric ruthenacyclobutane by <sup>1</sup>H NMR spectroscopy.<sup>10</sup> Complex **6** was isolated by our group from the reaction of **2** and diphenylacetylene.<sup>13</sup> Although the bonding in **6** lies between a ruthenacyclobutane and a ruthenium–olefin complex, it is suggestive of a side-bound olefin intermediate. However, no studies have synthesized ruthenium–olefin adducts bearing *N*-heterocyclic carbenes (NHCs), ligands that enable the high activity, stability, and selectivity observed for chiral and achiral olefin metathesis catalysts.

To study olefin binding in NHC-based ruthenium catalysts, we chose to explore 1,2-divinylbenzene (**8**) as a chelating ligand precursor due to its inability to undergo ring-closing metathesis and expected slow homodimerization.<sup>14</sup> Upon addition of **8** to a solution of **7** in benzene, two new species in a ratio of 2:3 are initially observed by <sup>1</sup>H NMR spectroscopy (eq 1). In CD<sub>2</sub>Cl<sub>2</sub>, both reaction products display six magnetically inequivalent Me groups and geminal olefinic protons that are significantly shifted upfield to 3.37–3.59 ppm in the <sup>1</sup>H NMR spectrum. These complexes were found to be competent metathesis catalysts at elevated temperatures.<sup>15</sup> We envisioned three possible structural isomers based on

**Scheme 1.** Initial Steps of the Mechanism of Olefin Metathesis



**4a** and **4b**: one isomer featuring a bottom-bound olefin (**9a**), a geometry similar to that of previously synthesized chelating *i*-Pr ether catalysts,<sup>16</sup> and two side-bound isomers in which the terminal methylene can either point away from (**9b**) or toward (**9c**) the NHC ligand (Figure 1).



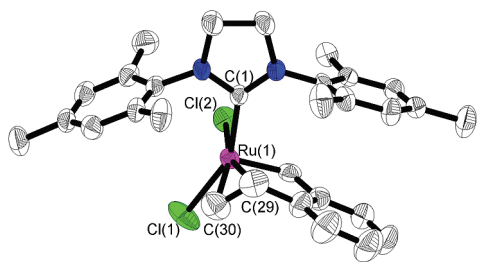
**Figure 1.** Structural isomers of **9**.

X-ray crystallographic analysis of crystals grown from slow diffusion of pentane into a CH<sub>2</sub>Cl<sub>2</sub> solution of **9** showed a single compound, **9b**, in which the olefin is coordinated to ruthenium cis to the NHC (Figure 2). The C(29)–C(30) olefin bond length in **9b** (1.331(4) Å)<sup>17</sup> is close to that of free styrene (1.3245(16) Å),<sup>18</sup> suggesting a weak Ru–olefin interaction. However, the Ru–C(29) and Ru–C(30) bond lengths of **9b** (2.228(4) and 2.185(3) Å) are shorter than those found in **5** (2.362(5) and 2.339(5) Å) and **6** (2.356(4) and 2.221(4) Å).

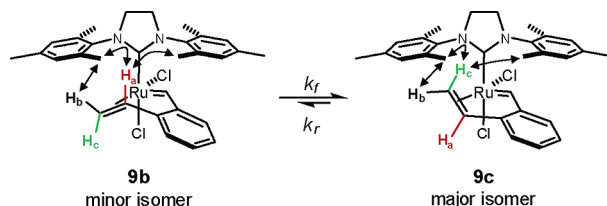
A series of NMR spectroscopy experiments was performed to elucidate the geometry of the two compounds formed in eq 1. In 2D NOESY experiments, cross-peaks are observed for the olefinic protons of each complex with Me groups on the mesityl rings (Figure 3). From consideration of internuclear distances in DFT-optimized structures,<sup>19</sup> these NOEs are consistent with side-bound complexes **9b** and **9c** but not bottom-bound compound **9a**. NOEs are observed for both isomers between H<sub>b</sub> and a Me group on the mesityl ring. Complex **9b** would be expected to have NOEs between H<sub>a</sub> and two Me groups on the mesityl rings; these are experimentally

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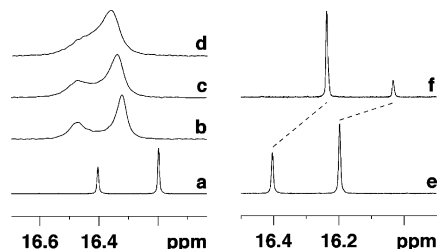
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**Figure 2.** X-ray crystal structure of **9b**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.



**Figure 3.** Structural assignments of solution isomers based on observed NOEs (indicated with arrows).



**Figure 4.** (a–d) Variable-temperature 400 MHz  $^1\text{H}$  NMR data for the benzylidene resonances of a sample of adduct **9** dissolved in  $\text{CDCl}_2\text{CDCl}_2$  at room temperature, with spectra recorded at 25 °C (a), 96 °C (b), 101 °C (c), and 106 °C (d). (e, f) 400 MHz  $^1\text{H}$  NMR spectra of the benzylidene resonances of olefin adduct **9** dissolved and recorded in  $\text{CD}_2\text{Cl}_2$  at 25 °C (e) and at  $-30$  °C (f). The high field resonance is assigned to isomer **9c**.

observed for the minor isomer. For compound **9c**, NOEs would be expected between  $\text{H}_c$  and two Me groups on the mesityl rings of the NHC and are observed for the major isomer. On the basis of this spectroscopic evidence, we assign **9b** as the minor isomer and **9c** as the major isomer observed in solution.

Two-dimensional EXSY experiments reveal two dynamic exchange processes in complex **9** at 25 °C.<sup>20</sup> The first, observed only for isomer **9c**, is an *o*-Me group exchange ( $k = 0.03 \text{ s}^{-1}$ ) consistent with Ru– $\text{C}_{\text{NHC}}$  bond rotation.<sup>21</sup> The second process is **9b**  $\leftrightarrow$  **9c** interconversion, evidenced by exchange between all resolved **9b** and **9c** resonances. The forward rate constant ( $k_f$ ) for this process was determined to be  $0.08 \pm 0.01 \text{ s}^{-1}$ , which corresponds to  $\Delta G_{298}^\ddagger = 18.9 \pm 0.1 \text{ kcal/mol}$ .

Variable-temperature  $^1\text{H}$  NMR experiments of compounds **9b** and **9c** in  $\text{CDCl}_2\text{CDCl}_2$  show coalescence of the benzylidene peaks at approximately 110 °C (Figure 4a–d). An Eyring analysis of the temperature-dependent forward rate constants, obtained from line shape analysis, was used to estimate the activation parameters. These are  $\Delta H^\ddagger = 21.4 \pm 0.6 \text{ kcal/mol}$ ,  $\Delta S^\ddagger = 7.5 \pm 1.8 \text{ eu}$ , and, therefore,  $\Delta G_{298}^\ddagger = 19.1 \pm 0.1 \text{ kcal/mol}$ , which is consistent with the EXSY-derived value.

Given the relatively high barrier to interconversion, we attempted to acquire a  $^1\text{H}$  NMR spectrum at low temperature of the single compound identified by X-ray crystallography. Crystals dissolved in  $\text{CD}_2\text{Cl}_2$  at  $-30$  °C showed benzylidene protons in a 5:1 **9b**:**9c** ratio as compared to the room temperature ratio of 2:3 (Figures 4e,f). Although not conclusive,<sup>22</sup> this is additional evidence for the **9b**/**9c** assignment described above.

In summary, we have developed a model system to study ruthenium–olefin complexes relevant to the mechanism of olefin metathesis. Our studies of the reaction between 1,2-divinylbenzene (**8**) and catalyst **7** have shown that two ruthenium–olefin adducts are formed and undergo dynamic interconversion. On the basis of observed NOEs and a low-temperature crystal dissolution experiment, we assign the two isomers as side-bound olefin adducts **9b** and **9c**. No evidence for a bottom-bound Ru–olefin adduct has been observed thus far; however, further experiments must be conducted to examine the implications and generality of these results for the mechanism of olefin metathesis. Investigations of chiral and achiral ruthenium catalysts with substituted 1,2-divinylbenzenes and other dienes are currently underway.

**Acknowledgment.** The authors thank Lawrence M. Henling and Dr. Michael W. Day for X-ray crystallography data, John Keith for invaluable assistance with theoretical calculations, and Materia, Inc. for generous donation of complex **2**. D.R.A. was supported by NDSEG and NSF predoctoral fellowships. D.J.O. thanks the Mellon Foundation for financial support. This research was also supported by the National Science Foundation.

**Supporting Information Available:** Experimental procedures, theoretical calculations, and full characterization of **9**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA0618090