

$\alpha,\beta$ -(C–C–C) Agostic bonds in transition metal based olefin metathesis catalyses†Cherumuttathu H. Suresh<sup>\*a,b</sup> and Mu-Hyun Baik<sup>\*a</sup><sup>a</sup> Department of Chemistry and School of Informatics, Indiana University, Bloomington, Indiana, 47405, USA<sup>b</sup> Division of Computational Modeling and Simulation, Regionnal Research Laboratory (CSIR), Trivandrum, 695019, India

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An  $\alpha,\beta$ -(C–C–C) agostic bond is found to provide the additional stabilization needed to make the formally 14-electron metallacyclobutane intermediate lower in energy than its 16-electron alkylidene analogue during olefin metathesis catalysis.

Agostic interactions<sup>1</sup> are widely recognized as key electronic features in many transition metal catalyzed C–H activation reactions.<sup>2–4</sup> Donation of  $\sigma$ -electron density from an otherwise inert C–H bond to an electron-deficient metal center can polarize the C–H bond and ultimately lead to its activation. Much less is known about similar interactions involving C–C bonds.<sup>5–8</sup> Intuitively, C–C bonds are good candidates for metal induced polarization because their bond energies of typically 80–90 kcal mol<sup>-1</sup> are  $\sim$ 10 kcal mol<sup>-1</sup> lower than those of typical C–H bonds. Recently, one of us proposed two  $\alpha$ -CC agostic bonds and a carbene-like C2-carbon<sup>9</sup> to be present in the ruthenacyclobutane intermediate of the migratory insertion step in the dissociative olefin metathesis reaction catalyzed by Grubbs' catalyst.<sup>10</sup> Our detailed electronic structure analysis now reveals a distinctively different picture implicating a single  $\alpha,\beta$ -(C–C–C) agostic bond to be the dominating electronic feature. Our studies indicate that this so far overlooked bonding type is present in a number of structural and functional analogues of the Ru-catalyst.

Fig. 1 shows the computed structures of the metallacyclobutane intermediates that are found as intermediates of the olefin metathesis catalysis. Complex **1** has been proposed by many as an intermediate in the dissociative mechanism<sup>9–11</sup> of Grubbs' first generation catalyst and complex **2** is its logical analogue for the second generation catalyst.<sup>12</sup> Standard electron counting rules classify the metallacyclobutane as formally a 14-electron species with a highly electron-deficient Ru(IV)-d<sup>4</sup> center. For that reason, many think of the metallacyclobutane as a transition state, whereas a number of computational studies identify it to be an intermediate that is usually *more stable* than the olefin adduct.<sup>9,13–16</sup> Very recently<sup>17</sup> the ruthenacyclobutane was

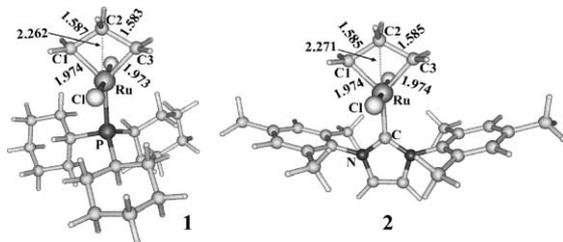


Fig. 1 DFT optimized structures of the ruthenacyclobutane intermediates catalyzing olefin metathesis: **1** = Grubbs' first generation catalyst; **2** = Grubbs' second generation catalyst (bond lengths in Å).

† Electronic supplementary information (ESI) available: Computational details, additional comments and Cartesian coordinates of all structures. See <http://dx.doi.org/10.1039/b508192k>

detected directly as an intermediate. Intuitively, it is difficult to accept that the immediate product of migratory insertion is lower in energy than the olefin complex, formally a 16-electron species. Our work confirms, however, in agreement with previous calculations that both complexes **1** and **2** are not only well-defined intermediates but are electronically also notably more stable by 7.4 and 9.2 kcal mol<sup>-1</sup>, respectively, than the olefin adducts. This counter intuitive trend is the result of an additional 4-center-2-electron interaction, an  $\alpha,\beta$ -(C–C–C) agostic bond, involving the donation of  $\sigma$ -electron density from the propylene moiety to the Ru-center to increase the electron count by 2 electrons and to formally give a 16-electron complex. Thus, in this special situation, the propylene ligand can formally be seen as a six-electron donor.

Bonding in metallacyclobutane was discussed qualitatively elsewhere.<sup>18</sup> Therefore, we limit our discussion to features promoting the new agostic bond. Fig. 2 shows a simplified MO-diagram of (PH<sub>3</sub>)Cl<sub>2</sub>Ru-1,3-(CH<sub>2</sub>)<sub>3</sub>, **3**, a model for **1**, where the neutral (PH<sub>3</sub>)Cl<sub>2</sub>Ru fragment is combined with a neutral propylene unit. The metal fragment containing a Ru(II)-d<sup>6</sup> center shows three occupied M–L antibonding MOs of d<sub>xy</sub>, d<sub>yz</sub> and d<sub>xz</sub> character, MOs 29, 33 and 34 on the left hand side of Fig. 2. The remaining two MOs of the M–L antibonding set are unoccupied.<sup>19</sup> There are three important fragment MOs on the neutral propylene ligand: The in-phase combination of mainly p<sub>x</sub> orbitals of the terminal carbon atoms forms

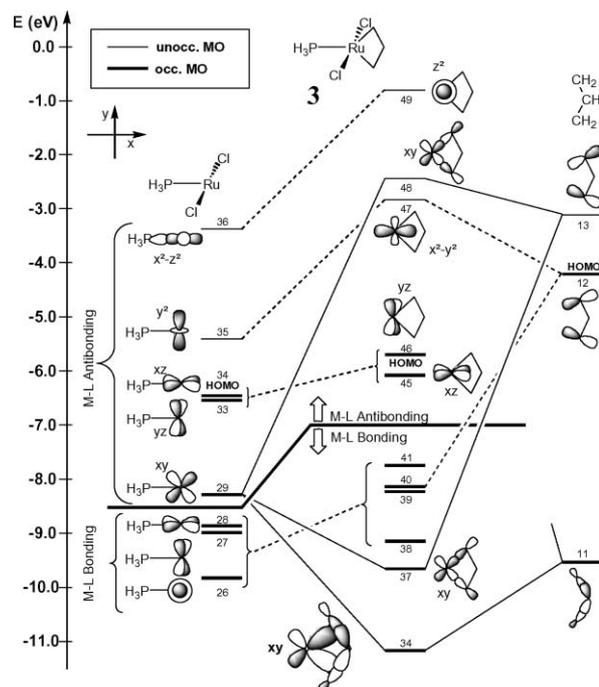
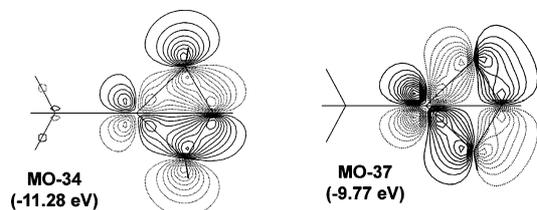


Fig. 2 MO-Diagram describing metallacycle formation. The MO responsible for the  $\alpha,\beta$ -(C–C–C) agostic bond is MO034.

the HOMO, whereas their out-of-phase combination gives the LUMO. From the two symmetry adapted linear combinations (SALCs) of the two C–C  $\sigma$ -bonds, only one (MO-11) is shown in Fig. 2. The MO-diagram illustrates clearly how the propylene fragment adds oxidatively to the Ru(II) center to give the Ru(IV) containing metallacycle in complex **3**, by utilizing the empty propylene MO-13 and the filled Ru(II)- $d_{xy}$  orbital (MO-29). The in-phase combination promoting the M–C bond (MO-37) is doubly occupied in complex **3**, whereas the anti-bonding combination remains empty. As a result, only 2 occupied MOs remain in the M–L antibonding subspace. Interestingly, we also found a strong bonding interaction between the propylene-based MO-11 and the Ru- $d_{xy}$  orbital to give the low-lying MO-34 (Fig. 2). Thus, it is one of the two SALCs of the two C–C  $\sigma$ -bonds that interacts with the metal  $d_{xy}$  orbital to give the  $\alpha,\beta$ -(C–C) agostic bond. The contour plot of MO-34 (Fig. 3) underlines clearly how strong and well-defined this interaction is. To illustrate the difference between this agostic interaction and one that promotes a usual Ru–C  $\sigma$ -bond, the contour plot of MO-37 is also shown in Fig. 3. The p-orbitals of the terminal carbon atoms involved in bonding in each of the two MOs are practically orthogonal to each other.



**Fig. 3** Contour plots of MOs 37 and 34. Contours are drawn at an interval of 0.025 au.

A consequence of this electronic feature is the observed distortion of the metallacyclobutane and a significant activation of the C–C bonds. The propylene moiety in both **1** and **2** display elongated C–C bonds of 1.585 Å that are  $\sim 0.07$  Å longer than a typical C–C single bond. This structure is notably different from a classical geometry, for example calculated for a 16-electron bisphosphine metallacyclobutane<sup>9</sup> ( $\text{PH}_3$ )<sub>2</sub>Cl<sub>2</sub>Ru(C<sub>3</sub>H<sub>6</sub>) with C–C distances of 1.511 Å. This phenomenon is not restricted to Ru or to reactive, transient intermediates. A selected few examples of early transition metal complexes<sup>20–23</sup> that exhibit the  $\alpha,\beta$ -(C–C) agostic bond, which were previously not recognized as such, are shown in Table 1. Interestingly, all complexes are well-known olefin metathesis catalysts, supporting the view that the  $\alpha,\beta$ -(C–C) agostic bond is a generally applicable electronic feature of C–C activation.

A direct  $\sigma$ -type interaction between the C2-carbon and the metal center is highly unlikely given the enforced orientation of the  $sp^3$ -hybridized carbon, but the formal Mayer bond order<sup>24</sup>  $M_{\text{BO}}$  between C2 and the metal center provides an acceptable quantitative measure for the agostic interaction. We note that

**Table 1** Complexes with  $\alpha,\beta$ -(C–C) agostic bonds. Computed bond lengths are given in Å. The agostic bonds are indicated in the structure with an arrow

	M–C1	C1–C2	C2–C3	M–C2	$M_{\text{BO}}$
<b>4</b> <sup>18</sup>	2.126	1.555	1.587	2.527	0.147
<b>5</b> <sup>19</sup>	2.191	1.570	1.642	2.543	0.189
<b>6</b> <sup>20</sup>	2.160	1.577	1.642	2.488	0.216
<b>7</b> <sup>21</sup>	2.087	1.600	1.602	2.393	0.314

only the C2-based orbital components of the C1–C2/C2–C3  $\sigma$ -bonds will be taken into account, whereas the C1 and C3-based orbital components of the  $\sigma$ -bond will be attributed to the M–C1/M–C3 bond order. In other words, only two of the 4-center-2-electron interactions are considered in this formal assignment of bond orders. For complexes **1** and **2** bond orders of 0.213 and 0.199 are found, respectively, which is consistent with the presence of a significant electronic interaction.<sup>25</sup> In the simplistic model **3**, a bond order of 0.252 is computed. Both DFT-optimized bond lengths and bond orders of all complexes examined are given in Table 1. In all complexes the C1–C2 and C2–C3 bonds are approximately 1.6 Å and the Ru–C2 distances are short, ranging from 2.40 to 2.55 Å. The computed  $M_{\text{BO}}$  values range from 0.147 to 0.314 and are much higher than what is found in typical agostic C–H complexes, such as  $\text{Cl}_3\text{Ti}(\text{CH}_2\text{CH}_3)((\text{CH}_3)_2\text{PC}_2\text{H}_4\text{P}(\text{CH}_3)_2)$ , where the formal  $\text{M} \cdots \text{C}$  bond order of 0.111 is computed. In Table 1, the new agostic bonding type has been indicated with an arrow originating from an arc that connects the two  $\sigma$ -bonds to illustrate the underlying electronic structure outlined above.

For the metal center to promote the CCC-agostic bond, it is crucial that the  $d_{xy}$  orbital is energetically accessible, that is it must be one of the lowest frontier orbitals of the metal fragment, as shown on the left hand side of Fig. 2. This MO-ordering, in turn, can only be achieved by leaving the equatorial coordination sites *trans* to M–C1 and M–C3 vectors empty. In the Grubb's catalyst, this feature is enforced by sterically bulky carbene and phosphine ligands, whereas the complexes listed in Table 1 make use of other structural features to enforce coordination geometries that will enable the formation of the  $\alpha,\beta$ -(C–C) agostic bond. More detailed and quantitative studies aimed at discovering strategies for controlling the reactivity of transition-metal based metathesis catalysts that exploit the new electronic feature are currently underway in our laboratories.

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