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Z-Selectivity in Olefin Metathesis with Chelated Ru Catalysts: Computational Studies of Mechanism and Selectivity

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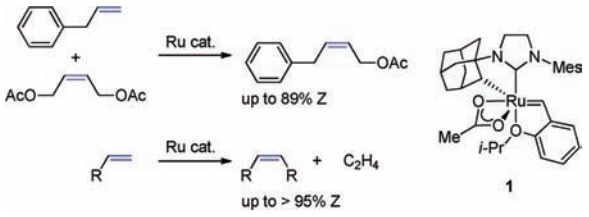
Supporting Information

ABSTRACT: The mechanism and origins of *Z*-selectivity in olefin metathesis with chelated Ru catalysts were explored using density functional theory. The olefin approaches from the "side" position of the chelated Ru catalysts, in contrast to reactions with previous unchelated Ru catalysts that favor the bottom-bound pathway. Steric repulsions between the substituents on the olefin and the N-substituent on the N-heterocyclic carbene ligand lead to highly selective formation of the *Z* product.

Olefin metathesis is a powerful tool for the formation of C−C double bonds in organic synthesis and materials chemistry.[1] While most catalysts favor the formation of the thermodynamically more stable (*E*)-olefins, recent advances in catalyst design have led to highly *Z*-selective olefin metathesis with Mo and W catalysts[2] and up to 51% *Z*-selectivity in ring-opening metathesis polymerization with O-chelated Ru phosphine catalysts.[3] *Z*-Selective cross-metathesis reactions have now been achieved with Ru catalysts **1** containing a chelating N-heterocyclic carbene (NHC) ligand (Scheme 1).[4,5]

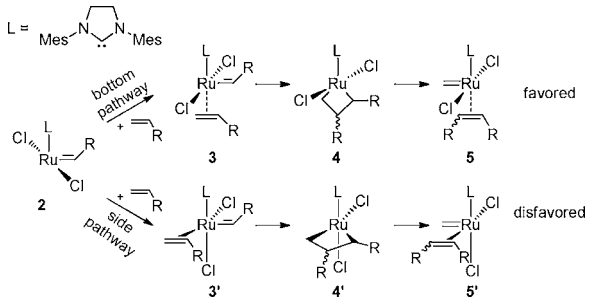
Scheme 1. *Z*-Selective Olefin Metathesis with Ru Catalyst 1[4]



These new catalysts dramatically extend the scope of olefin metathesis to produce (*Z*)-olefins selectively. The *Z*-selectivities with Mo and W catalysts have been attributed to the difference in the size of the two apical ligands of the incipient metallacyclobutane complex.[2] In the case of Ru, Torker et al.[3] have shown the steric interaction between the sulfonate anion and cyclic alkene substituents to have a controlling influence on *E*/*Z*-selectivity. The mechanism and origins of *Z*-selectivity with chelated Ru catalyst **1** containing Ru−C bonds have not been explored.

The mechanism of olefin metathesis employing previous unchelated Ru catalysts with phosphine or NHC ligands has been investigated extensively by computational studies from various research groups.[6−18] The generally accepted mechanism (Scheme 2) involves a 14-electron Ru−alkylidene complex **2** as

Scheme 2. Bottom- and Side-Bound Pathways of Olefin Metathesis with Unchelated Ru Catalysts



the active catalyst, which binds to an olefin molecule to form a Ru−olefin complex. The olefin may bind to the bottom position [i.e., trans to the NHC ligand (**3**)] or the side position [i.e., cis to the NHC ligand (**3′**)]. Low-temperature studies of metallacycles formed from Ru catalysts with NHC ligands are most consistent with a bottom-bound metallacycle.[19] Previous density functional theory (DFT) studies suggested the bottom-bound pathway to be more favorable with unchelated Ru catalysts[8c,7c,17b] and the formation of the *E* products to be favored both kinetically and thermodynamically.[8d,17b]

We performed DFT calculations to investigate the mechanism and origins of *Z*-selectivity with the aforementioned chelated Ru catalysts. The pivalate-substituted catalyst was the first reported Ru catalyst that showed up to 95% *Z*-selectivity. Subsequent studies[4c] indicated that the acetate-substituted catalyst **1** shows similar reactivity and selectivity (Scheme 1) and that the turnover number and *Z*-selectivity are greatly improved by exchanging the carboxylate for a nitrato-type ligand. We employed the acetate catalyst **1** in this study as a model of carboxylate-based catalysts. B3LYP and a mixed basis

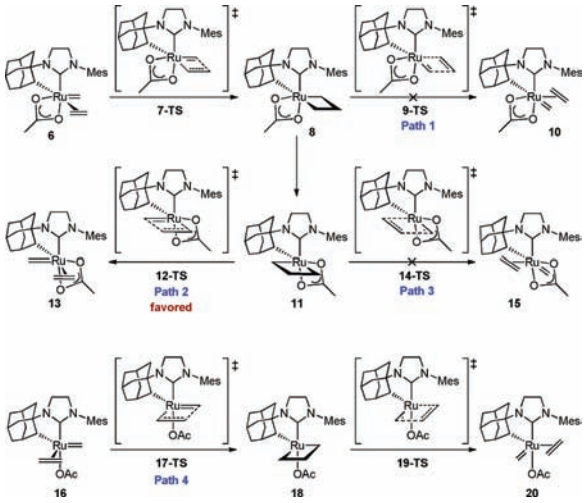
Received: November 18, 2011
Published: January 9, 2012

dx.doi.org/10.1021/ja2108728 | J. Am. Chem.Soc. 2012, 134, 1464−1467

set of LANL2DZ for Ru and 6-31G(d) for other atoms were used in geometry optimizations. Single-point energies were calculated with M06 and a mixed basis set of SDD for Ru and 6-311+G(d,p) for other atoms.[20] Solvation energy corrections were calculated using the SMD model with THF as the solvent. All of the calculations were performed with Gaussian 09.[21]

Both the side- and bottom-bound mechanisms were investigated for the degenerate reaction of ethylene with catalyst **1**. Because of the unsymmetrical nature of the chelating ligand and the possibility that acetate could be monodentate or bidentate, there are four possible pathways for the side-bound attack of olefin (Scheme 3). In the pathways involving bidentate acetate, the Ru complex adopts an octahedral geometry after binding to the olefin. After the formation of metallacyclobutane intermediate **8**, direct cleavage of the metallacycle would lead to Ru–alkylidene complex **10** (path 1), in which the alkylidene is trans to the chelating adamantyl group. Alternatively, **8** could isomerize to complex **11**, leading to two different metallacycle cleavage pathways (paths 2 and 3) that would form Ru–alkylidene complexes **13** and **15**, respectively. In path 4 involving monodentate acetate, the Ru complexes would adopt similar geometries as in the reactions with unchelated dichloro-Ru catalysts.[8c] Similarly, for the bottom-bound case there are three pathways involving bidentate acetate and one with monodentate acetate.[22]

Scheme 3. Possible Side-Bound Pathways of Olefin Metathesis with Chelated Ru Catalyst 1



We computed the transition states (TSs) and intermediates for all eight possible pathways. The most favorable pathway for the side-bound attack is path 2, which involves isomerization of the metallacyclobutane intermediate **8** to **11**. Ru–alkylidene complexes **10** and **15**, in which the alkylidene is trans to the strong σ-donor adamantyl group, are highly unstable. The corresponding TSs (**9-TS** and **14-TS**) leading to these high-energy complexes are disfavored by 8.8 and 11.3 kcal/mol, respectively, relative to **12-TS** in the lowest-energy reaction pathway (path 2). The monodentate metallacyclobutane intermediate **18** is more stable than the bidentate intermediates **8** and **11**. However, the bidentate TSs are more stable than the corresponding monodentate TSs.[22] Similarly, the most favorable bottom-bound pathway also involves isomerization of the metallacyclobutane intermediate and eventually forms a Ru–product complex in which the alkylidene is cis to both the adamantyl group and the NHC ligand. The acetate also prefers to be bidentate in the bottom-bound TSs.[22]

The free energies and enthalpies of all TSs and intermediates in the most favorable side- and bottom-bound pathways are summarized in the energy surfaces shown in Figure 1. All energies are relative to the active catalyst, 14-electron Ru–alkylidene complex **21**. Binding of ethylene to **21** is exothermic in both the bottom- and side-bound pathways. In the side-bound pathway (shown in blue in Figure 1), formation of the metallacyclobutane requires a very low barrier (**7-TS**, $\Delta G^{\ddagger}$ = 4.1 kcal/mol) and leads directly to octahedral intermediate **8** in which the acetate is bidentate. Complex **8** easily isomerizes to monodentate intermediates **18** and **18′** and another bidentate metallacycle, **11**.[23] Cleavage of the metallacycle requires an activation free energy of 18.7 kcal/mol (**12-TS**) with respect to the most stable metallacycle intermediate (**18**). Dissociation of the olefin product leads to 14-electron Ru–alkylidene complex **22**, an isomer of **21**. Complex **22** may serve as an active catalyst that undergoes a catalytic cycle to regenerate **21**.

In the bottom-bound pathway (shown in green in Figure 1), the Ru–olefin π complex **24** is 6.3 kcal/mol more stable than the corresponding side-bound complex **6**, but the activation barrier leading to the metallacycle (**25-TS**, $\Delta G^{\ddagger}$ = 14.5 kcal/mol) is much higher than that in the side-bound pathway (**7-TS**, $\Delta G^{\ddagger}$ = 4.1 kcal/mol). Intrinsic reaction coordinate calculations showed that **25-TS** leads directly to monodentate metallacyclobutane intermediate **26**. No bidentate metal-

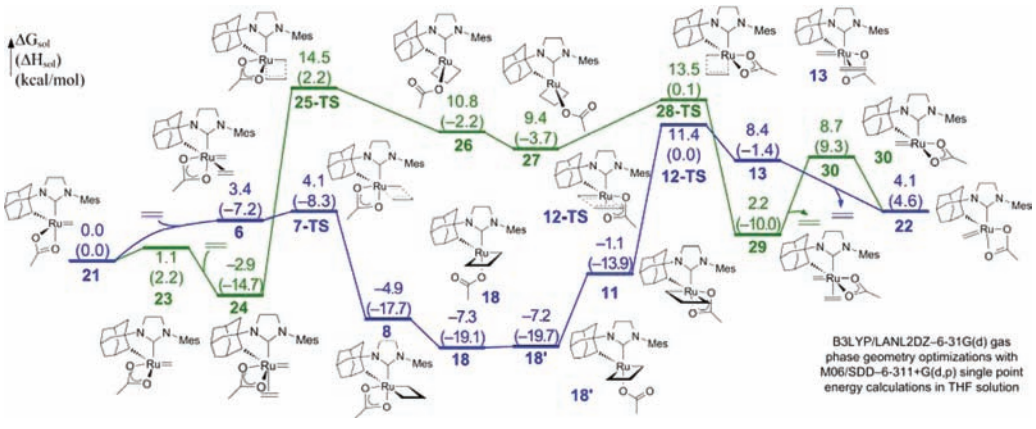


Figure 1. Free energy profiles of the side-bound (blue) and bottom-bound (green) pathways of olefin metathesis with chelated Ru catalyst **1**.

dx.doi.org/10.1021/ja2108728 | J. Am. Chem.Soc. 2012, 134, 1464–1467

lacyclobutane intermediates in the bottom-bound pathways were located in geometry optimizations. The metallacycles in the bottom-bound pathway (**26** and **27**) are much less stable than those in the side-bound pathway (**8**, **11**, **18**, and **18′**). The second metathesis step in the bottom-bound pathway has a barrier similar to that in the first step (**28-TS**, $\Delta G^{\ddagger}$ = 13.5 kcal/mol). The overall barrier for the bottom-bound pathway is 3.1 kcal/mol higher than for the side-bound pathway.

The strong preference for the side-bound mechanism with the chelated catalysts is due to a combination of steric and electronic effects of the chelating NHC ligand. In the bottom-bound TSs (**25-TS** and **28-TS**, Figure 2), the alkylidene adopts

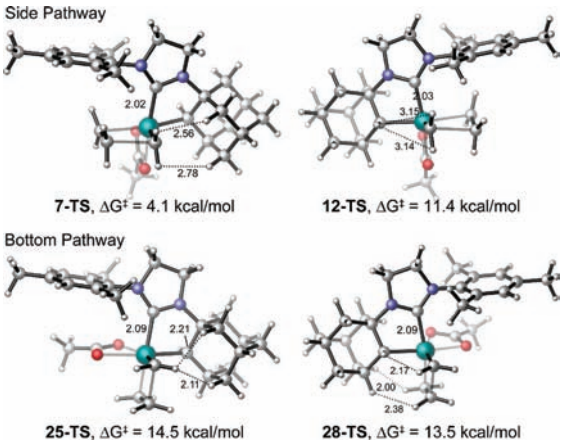


Figure 2. TS structures for the side- and bottom-bound pathways.

a horizontal conformation with one H atom on the alkylidene pointing toward the bulky chelating adamantyl group. Steric repulsions of the alkylidene and the olefin with the adamantyl group are observed in the bottom-bound TSs. In contrast, in the side-bound TSs (**7-TS** and **12-TS**, Figure 2), the alkylidene is vertical and the olefin is trans to the adamantyl group, and thus, no steric repulsions with the adamantyl group are present.

The bottom-bound TSs are also destabilized by electronic effects. Both the NHC and alkylidene are strong σ donors as well as π acceptors via back-donation from the metal d orbital to the empty π^* orbitals of the NHC and alkylidene. As a result of chelation, the conformation of the NHC is fixed in such a way that the π^* orbital of the NHC is in the same plane with the Ru−alkylidene bond. In the bottom-bound TSs, the alkylidene adopts a horizontal conformation (Figure 2), and its π^* orbital is oriented in the same plane as the π^* orbital of the NHC ligand. Thus, the same Ru d orbital is involved in the back-donation to the two π^* orbitals (Figure 3).[13,14] In the side-bound TSs, the alkylidene is vertical, and the π^* orbitals of the alkylidene and the NHC ligand are perpendicular to each other. The d → π^* back-donation involves two different d orbitals of the metal (Figure 3). The weaker back-donation in the bottom-bound TSs destabilizes these structures and leads to longer Ru−NHC bond distances. The Ru−C_{NHC} distances in the bottom-bound TSs are ∼2.09 Å, which is considerably longer than those in the side-bound TSs (∼2.03 Å; see Figure 2). In reactions with previous unchelated Ru−NHC catalysts, the NHC is parallel to the Ru−alkylidene bond, and the π^* orbitals of the NHC and the alkylidene are not in the same plane in either the side- or bottom-bound TS.[13] Thus, no such electronic effects that destabilize the bottom-bound TS are present with unchelated Ru catalysts.

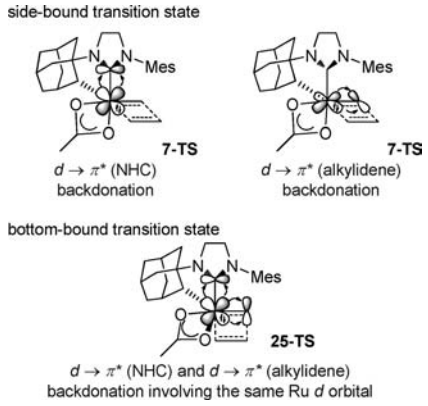
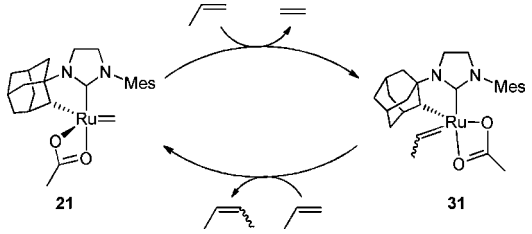


Figure 3. Back-donation in the side- and bottom-bound TSs.

The bidentate anionic ligand also plays an important role in destabilizing the bottom-bound TSs. In the unchelated dichloro-Ru catalyst, the two chlorides are trans in the favored bottom-bound pathway and cis in the side-bound pathway (Scheme 2). Replacing dichloro with acetate constrains the anionic ligand to bind cis to Ru. Previous theoretical studies suggested that polar solvents stabilize the side-bound complexes.[8c,17a] With chelation, the bottom- and side-bound TSs have similar dipole moments, so the solvent effects are small.

The side-bound mechanism that occurs with the chelated Ru catalyst offers unique control of the *Z*-selectivity through steric interactions between the olefin substituents and the NHC ligand. In contrast, metathesis with unchelated Ru catalysts involves bottom attack of the olefin (i.e., anti to the NHC ligand), and thus, the ligand effects on the *Z*/*E*-selectivity are minimal.[3] To investigate the origin of the *Z*-selectivity with the chelated catalyst, the possible pathways leading to the *Z* and *E* products in the homodimerization of propene were computed. Since the *Z*-selectivity is kinetically controlled,[4c] only TSs involved in the *Z*/*E*-selectivity-determining process [i.e., the transformation from **31** to **21** (Scheme 4)] were considered.

Scheme 4. Catalytic Cycle for Propene Homodimerization



The different orientations of methyl groups on the metallacyclobutane lead to eight possible side-bound pathways and eight possible bottom-bound pathways. As in the metathesis of ethylene, the side-bound mechanism is strongly preferred. The most favorable bottom-bound pathway requires an 8.2 kcal/mol higher activation free energy than the side-bound pathway. Both (*Z*)- and (*E*)-olefin products are formed via side-bound TSs (Figure 4).

Both TSs in the *E*-selective pathway (**34-TS** and **35-TS**) are less stable than those in the *Z*-selective pathway (**32-TS** and **33-TS**). In the *E*-selective TSs, one of the methyl groups that would be in the (*E*)-2-butene product points toward the mesityl group of the ligand. Since chelation of the ligand constrains the mesityl group to be directly above the forming

dx.doi.org/10.1021/ja2108728 | *J. Am. Chem.Soc.* 2012, 134, 1464−1467

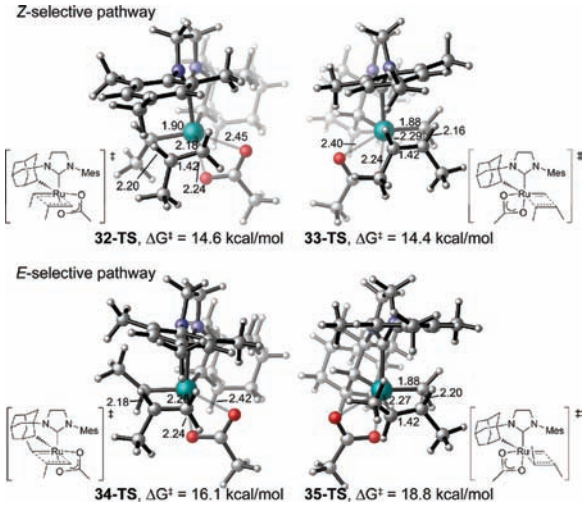


Figure 4. TSs of the most favorable pathways leading to *Z* and *E* products with catalyst **1**.

metallacyclobutane, steric repulsions between the methyl substituent and the ligand are observed in both **34-TS** and **35-TS**. In the *Z*-selective TSs, both methyl substituents point away from the mesityl group, and the steric repulsions with the ligand are avoided. The overall activation barrier for the formation of the *E* product is 4.3 kcal/mol higher than that for the *Z* product, in agreement with the observed *Z*-selectivity.[24]

In summary, DFT calculations have shown that olefin metathesis with chelated Ru catalysts occurs via a side-bound mechanism in which the olefin attacks cis to the NHC and trans to the chelating adamantyl group. The preference for the side-bound mechanism is attributed to a combination of steric and electronic effects of the chelated catalyst. The side-bound mechanism enables steric influences of the NHC ligand to control the selective formation of (*Z*)-olefin products.

■ ASSOCIATED CONTENT

Supporting Information

Details of computational methods, additional computational results, and complete ref 21. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

We thank the National Science Foundation (K.N.H., CHE-1059084; R.H.G., CHE-1048404) and the Natural Science Foundation of China (X.F.X., 21103094) for financial support of this research and Yu Lan for helpful discussions. Calculations were performed on the Hoffman2 cluster at UCLA and the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by the NSF.

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(22) See the Supporting Information for details.

(23) The concerted TS for isomerization from **8** to **11** is 10.3 kcal/mol higher in energy than **18**.

(24) The predicted *Z*-selectivity is higher than observed experimentally. The (*E*)-olefin products may form via alternative pathways, e.g., the catalytic cycle involving decomposed Ru catalysts.