Supporting Information

Conformational Analysis of Olefin-Carbene Ru Metathesis Catalysts

Diego Benitez, Ekaterina Tkatchouk and William A. Goddard, III

Contribution from the Materials and Process Simulation Center, Beckman Institute (139-74), Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

wag@wag.caltech.edu
**Computational Methods.** Calculations were performed on all systems using density functional theory (DFT) with the B3LYP, M06 and M06-L functionals, as implemented in Jaguar 7.0 (release 207).\(^1\) B3LYP utilizes both exact Hartree-Fock (HF) exchange and corrections (generalized gradient approximation) to the Slater exchange functional, the Becke three-parameter functional (B3) with the Becke gradient correction,\(^2\) the Vosko-Wilk-Nusair exchange functional,\(^3\) and the correlation functional of Lee, Yang, and Parr (LYP).\(^4\)

All calculations used the Hay and Wadt small core-valence relativistic effective-core-potential\(^5\) (ECP) to describe the 1s-3d core electrons of the ruthenium atom, leaving the outer 16 electrons (4s, 4p, 4d, 5s, etc.) to be treated explicitly.

Our previous results showed that the LACVP** basis set produces geometries in good agreement with experiment and that the extended LACV3P++** basis set\(^6\) describes properly the energy of intermediates relevant to olefin metathesis. Here LACVP** was used for all geometry optimizations and LACV3P++**(2f) for energies. LACV3P++**(2f) utilizes the LACV3P++** basis set as implemented in Jaguar plus a double-zeta f-shell with exponents reported by Martin and Sundermann.\(^7\) All electrons were described for all other atoms using the 6-31G** or 6-311++G** basis sets.\(^8\)

Every structure was optimized in the gas phase with the B3LYP and M06-L functionals as noted. For each B3LYP optimized structure, the analytic Hessian was calculated to obtain the vibrational frequencies, which in turn were used to obtain the zero point energies and free energy corrections (without translational or rotational components) to 298 K or as noted. Solvent corrections were based on single point self-consistent Poisson-Boltzmann continuum solvation calculations for CH\(_2\)Cl\(_2\) (\(\varepsilon = 8.93\) and \(R_0= 2.33\) Å) or benzene (\(\varepsilon = 2.284\) and \(R_0= 2.60\) Å) using the PBF\(^9\) module in Jaguar, which has been shown\(^10\) recently to give quite accurate results. (\(\varepsilon\) is dielectric constant and \(R_0\) is the solvent’s probe radius, see ref. 9 for more details).

Norbornene Ring-Opening Reaction. All structures were optimized with the M06-L functional in the gas phase and electronic energies were obtained using the M06 functional with the LACV3P++**(2f) basis set. Transition structures were located using B3LYP transition structures as initial geometries.

**References**
(6) The LACV3P basis set is a triple-zeta contraction of the LACVP basis set developed and tested at Schrödinger, Inc.
(e) Frisch, M. J.; Pople, J. A.; Binkley, J. S. J. Chem. Phys. 1984, 80, 3265.