Communications to the Editor

Methane Metathesis at a Cationic Iridium Center

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Received April 1, 1996

Recently, Arndtsen and Bergman reported[1] low-temperature hydrocarbon bond activation by a cationic iridium complex. In this reaction, the complex activates a hydrocarbon C−H bond, transfers the hydrogen atom to a methyl ligand, and ejects methane as a reaction product. The net result is a σ-bond metathesis reaction between $M-CH_3$ and $R-H$, where M is $Cp^*Ir(P(CH_3)_3)(CH_3)^+$ and $Cp^* = C_5(CH_3)_5$. Two specific mechanisms were proposed: (1) The metathesis proceeds through a four-center adduct between $M-CH_3$ and $R-H$, in which the hydrogen atom transfers from R to CH_3 while maintaining a long distance from iridium, a mechanism which has been observed for early transition metals.[2] (2) The hydrocarbon undergoes oxidative addition to the iridium atom, so that R and H are both directly bonded to the metal atom before the reductive elimination of methane, a mechanism which cycles the oxidation state of the iridium atom from Ir(III) to Ir(V) and back to Ir(III). Both mechanisms are illustrated in Scheme 1.[1] These two mechanisms are explored theoretically for the specific case where $R-H$ is methane and $M-CH_3$ is $CpIrPH_3CH_3^+$ ($Cp = C_5H_5$), a cationic complex which is a model system for the cationic complex studied by Arndtsen and Bergman.[1] The theoretical data show that the oxidative-addition mechanism is a low-energy pathway and that the four-center adduct mechanism is doubtful even at higher energies.

Theoretical calculations in this work have been performed using density functional theory (DFT), specifically the Becke three-parameter exchange functional[3] (B3) and the Lee−Yang−Parr correlation functional[4] (LYP). These B3LYP calculations have been carried out with the Gaussian 94 program.[5] The basis set for iridium is a modified version of Gaussian 94's LANL2DZ basis,[6] where the two outermost p functions have been replaced by a (41) split of the optimized iridium 6p function from Couty and Hall.[7] Cartesian d functions (six basis functions per d function) were employed for iridium. The standard LANL2DZ basis sets were chosen for the carbon,[8] hydrogen,[8] and phosphorus atoms.[9]

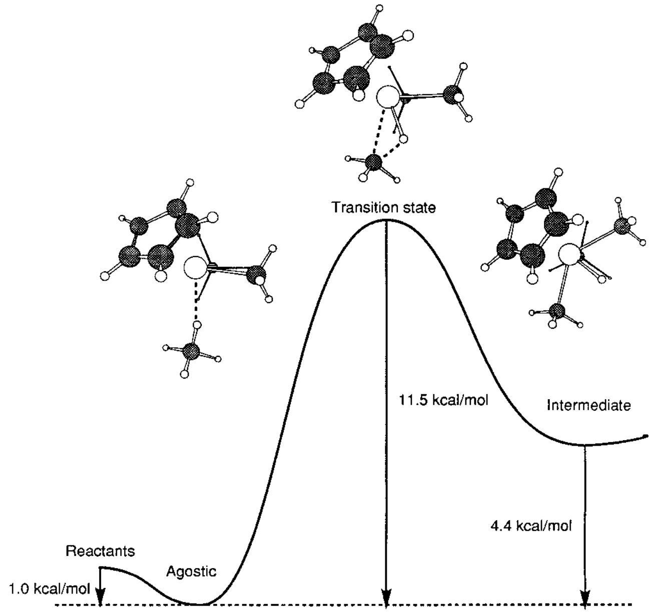

Figure 1. B3LYP energetics for oxidative-addition mechanism for methane metathesis. The agostic, transition state, and oxidative-addition intermediate are pictured above their respective places in the energy curve. The energy curve from the intermediate to the products is a reflection of the curve in this figure.

Scheme 1

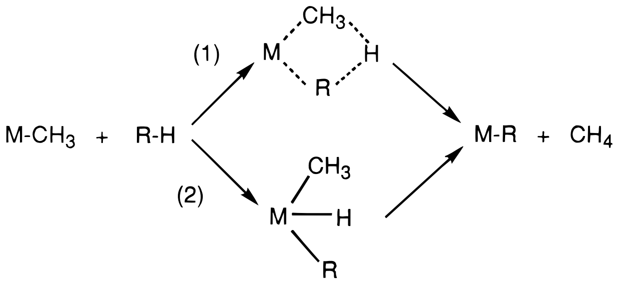

Table 1. Geometric Parameters for Stationary Points Along the Oxidative-Addition Mechanism[a]

	Ir−C	Ir−H	C−H
agostic	2.905	2.007	1.129
transition state	2.278	1.611	1.535
intermediate	2.177	1.567	2.194

[a] Distances in angstroms.

B3LYP geometry optimizations have been carried out for all stationary points along the oxidative-addition pathway (mechanism 2 above). This includes the reactants, an agostic structure in which the methane reactant is weakly bound to the iridium center, a transition state between the agostic and the oxidative addition intermediate, and the intermediate itself. Stationary points on this path are shown in Figure 1, along with the energetics of the mechanism. The path from the intermediate to the products is simply a reflection of the path from the reactants to the intermediate. Important geometric parameters for selected stationary points are shown in Table 1. The barrier to methane metathesis via the oxidative addition path is 11.5 kcal/mol.

Initial attempts at finding a four-center adduct or transition state for mechanism 1 above were unsuccessful, so more

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(1) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970. Earlier, Burger and Bergman (*J. Am. Chem. Soc.* **1993**, *115*, 10462) reported a similar complex which activated methane at higher temperatures.

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(4) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(5) Gaussian 94 (Revision B.1) Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T. A., Petersson, G. A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Cioslowski, J., Stefanov, B. B., Nanayakkara, A., Challacombe, M., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M. W., Andres, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. G., Binkley, J. S., Defrees, D. J., Bajer, J., Stewart, J. P., Head-Gordon, M., Gonzalez, C., and Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1995.

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S0002-7863(96)01057-8 CCC: $12.00

systematic means for examining the potential energy surface (PES) were employed. Using the B3LYP method, we searched for low-energy structures along the Ir−H coordinate. First, the geometry of the oxidative addition intermediate was used for a simple scan of the energy versus the Ir−H distance without reoptimization of the other degrees of freedom. The result was a monotonic increase in the energy for Ir−H distances up to at least 4.6 Å. Next, several of these structures along the Ir−H coordinate were allowed to relax the other degrees of freedom while holding the Ir−H distance fixed. This did not result in either a significant lowering of the energy or a significant change in the other geometric parameters. Finally, at different values for the Ir−H distance, scans were performed along the C−Ir−C coordinate to determine if narrowing the methyl−iridium−methyl angle resulted in any low-energy structures, which could occur if the structures from the Ir−H scan were local minima with respect to the other degrees of freedom. Again, the result was a monotonic increase in energy. Given these failures to locate a four-center adduct or transition state, it is reasonable to suppose that none exists in this region of the PES.

In early transition-metal systems, the metathesis must proceed through a four-center adduct (mechanism 1) because the metal has insufficient electrons to allow oxidative addition (mechanism 2). This is illustrated by the work of Rappé and Upton, whose theoretical work on scandium[10] reveals a four-center adduct with a methyl−scandium−methyl angle of about 77°. By contrast, our oxidative-addition intermediate has a methyl−iridium−methyl angle of 129°, and the angle remains large even as the hydrogen atom is pulled away from iridium, thereby preventing the iridium complex from stabilizing a four-center adduct. The same electron pair that is used for Ir−H bonding in the oxidative-addition mechanism exerts a repulsion which keeps the methyl−iridium−methyl angle large and precludes the four-center adduct mechanism.

These B3LYP calculations have elucidated a low-energy mechanism for the metathesis process between methane and $CpIrPH_3CH_3^+$, involving the oxidative addition of methane to the metal center. The theoretical data predicts that this pathway is preferred over a pathway without Ir−H bonding. Future applications include theoretical studies of this metathesis mechanism for other hydrocarbons, and in fact, such calculations are in progress for ethylene and acetylene.[11]

Acknowledgment. We thank the National Science Foundation (Grant No. CHE 94-23271) and the Robert A. Welch Foundation (Grant No. A-648) for financial support. This research was conducted in part with use of the Cornell Theory Center, a resource for the Center for Theory and Simulation in Science and Engineering at Cornell University, which is funded in part by the National Science Foundation, New York State, and IBM Corporation.

JA961057H

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[11] Strout, D. L.; Zaric, S.; Niu, S.; Hall, M. B. Unpublished results. Also, calculations are in progress that employ higher levels of theory, e.g. configuration interaction and coupled-cluster.