

## Cleavage of Both C(sp<sup>3</sup>)–C(sp<sup>2</sup>) Bonds of Alkylidenecyclopropanes: Formation of Ethylene–Osmium–Vinylidene Complexes

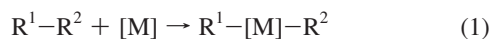
Ruth Castro-Rodrigo,<sup>†</sup> Miguel A. Esteruelas,<sup>\*,†</sup> Ana M. López,<sup>\*,†</sup> Fernando López,<sup>§</sup> José L. Mascareñas,<sup>\*,‡</sup> Montserrat Oliván,<sup>†</sup> Enrique Oñate,<sup>†</sup> Lucía Saya,<sup>‡</sup> and Lara Villarino<sup>‡</sup>

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain, Departamento de Química Orgánica, Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain, and Instituto de Química Orgánica General-CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

Received October 30, 2009; E-mail: maester@unizar.es; amlopez@unizar.es; joseluis.mascareñas@usc.es

The cleavage of C–C bonds with the help of transition-metal complexes is a field of much current interest because of its potential applications in organic synthesis and petroleum and pharmaceutical research.<sup>1</sup>

Splitting of C–C single bonds of acyclic hydrocarbons to afford metal complexes containing two different donor carbon ligands (eq 1) is a scarcely observed reaction.<sup>2</sup> Usually, such C–C activation requires either the attainment of aromaticity<sup>3</sup> or the use of a coordination auxiliary that brings the transition metal to the C–C bond.<sup>4</sup> Alternatively, specific C–C bond activations have been achieved under photochemical conditions.<sup>5</sup>



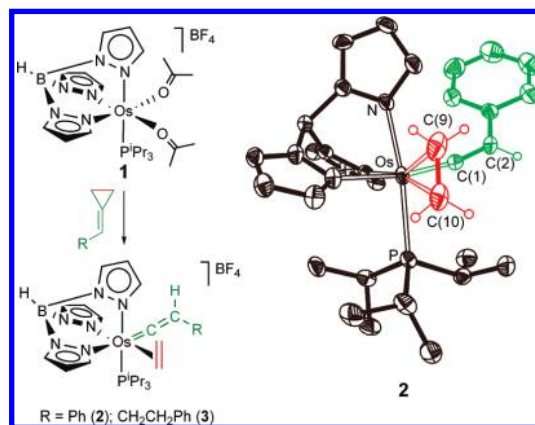
The activation of C–C single bonds of high-energy hydrocarbons such as strained three- or four-membered rings has been also described.<sup>6</sup> For instance, as early as 1955, Tipper reported the conversion of cyclopropane into platinumacyclobutane.<sup>7</sup> However, to our knowledge, splitting of cyclic hydrocarbons to give complexes with two independent carbon donor ligands is unknown.

Alkylidenecyclopropanes are stable, strained three-membered-ring compounds containing an exocyclic C=C bond that have enormous potential in organic synthesis.<sup>8</sup> While a wide range of metal-catalyzed processes involving these substrates has been reported,<sup>9</sup> the number of transition-metal complexes isolated is extremely scarce.<sup>10</sup> Recently, we have shown that alkylidenecyclopropanes containing a chelation assistant at the terminal carbon atom of the olefinic moiety undergo Os-promoted ring expansion.<sup>11</sup> Now we have discovered that in the absence of the coordination auxiliary, they can be cracked to ethylene and vinylidene units under very mild conditions to afford ethylene–osmium–vinylidene complexes (Scheme 1 and Figure 1).

Treatment of fluorobenzene solutions of the osmium complex [OsTp( $\kappa^1$ -OCMe)<sub>2</sub>(P<sup>i</sup>Pr<sub>3</sub>)]BF<sub>4</sub> [Tp = hydridotris(pyrazolyl)borate] (**1**) with 1.4 equiv of benzylidenecyclopropane for 30 min at room temperature leads to the quantitative formation of [OsTp(=C=CHPh)( $\eta^2$ -CH<sub>2</sub>=CH<sub>2</sub>)(P<sup>i</sup>Pr<sub>3</sub>)]BF<sub>4</sub> (**2**), which results from the release of the acetone molecules and the two-way split of the three-membered ring of the substrate. This unexpected complex was isolated as a brown solid in 71% yield. Under the same conditions, 3-phenylpropylidenecyclopropane gives [OsTp(=C=CHCH<sub>2</sub>CH<sub>2</sub>-Ph)( $\eta^2$ -CH<sub>2</sub>=CH<sub>2</sub>)(P<sup>i</sup>Pr<sub>3</sub>)]BF<sub>4</sub> (**3**) as a pink solid in 80% yield.

The X-ray structure of **2** proves the fragmentation of the ring into two pieces and the formation of the vinylidene and ethylene

Scheme 1



ligands. The former ligand is bound to the metal in a nearly linear fashion, with an Os–C(1)–C(2) angle of 169.2(3)° and Os–C(1) and C(1)–C(2) bond lengths of 1.841(3) and 1.312(5) Å, whereas the coordination of the latter one is almost parallel to the N–Os–P direction and symmetrical, with Os–C(9) and Os–C(10) distances of 2.216(4) and 2.232(4) Å and a C(9)–C(10) separation of 1.360(6) Å. These parameters agree well with those found in other osmium–vinylidene<sup>12</sup> and osmium–ethylene<sup>13</sup> complexes.

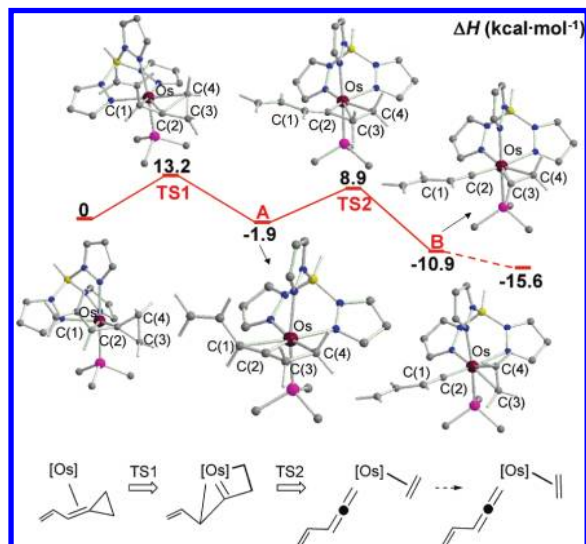


Figure 1. Energy profile for the fragmentation process. The H atoms of the pyrazolyl and PMe<sub>3</sub> groups have been omitted for clarity.

<sup>†</sup> Universidad de Zaragoza.

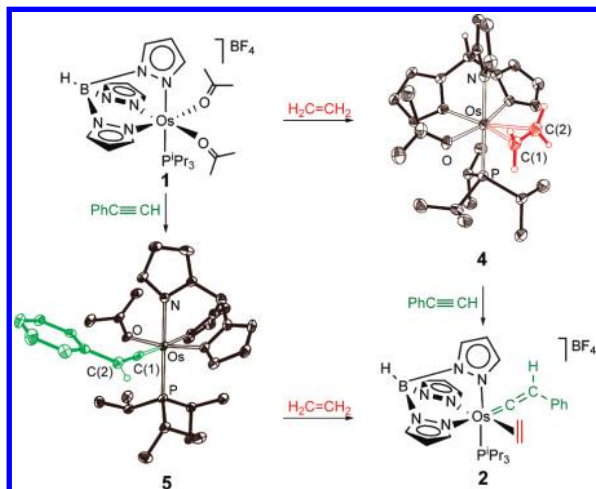
<sup>‡</sup> Universidade de Santiago de Compostela.

<sup>§</sup> Instituto de Química Orgánica General.

The fragmentation process was analyzed by density functional theory calculations (B3PW91/LANLZDZ) using allylidene-cyclopropane and  $\text{PMe}_3$  as models of alkylidene-cyclopropane and  $\text{P}^i\text{Pr}_3$ , respectively. Figure 1 shows the energy profile. Starting from  $\eta^2$ -olefin species, insertion of the metal center into one of the  $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^2)$  bonds of the three-membered ring [ $\text{C}(2)\text{--C}(4)$ ] induces the formation of the osmabicyclic intermediate **A**, which can be described as an osmacyclopropene stabilized by an ethylene chelation assistant. The  $\text{Os--C}(2)$  and  $\text{Os--C}(1)$  distances of 1.882 and 2.268 Å, respectively, compare well with those found by X-ray diffraction analysis for reported osmacyclopropene complexes<sup>14</sup> and support the double and single character of the bonds between the respective atoms. Intermediate **A** evolves into the reaction product by cleavage of the  $\text{C}(2)\text{--C}(3)$  bond through transition state **TS2**. This step requires the decoordination of  $\text{C}(1)$  and the coordination of  $\text{C}(3)$ . The resulting ethylene–Os–vinylidene rotamer **B**, in which the ethylene molecule is perpendicular to the  $\text{N--Os--P}$  direction, rearranges to the final product by a 90° rotation of the olefin. The first  $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^2)$  rupture is the rate-determining step for the reaction.

The ethylene–Os–vinylidene species are certainly thermodynamic sinks. These compounds can be also prepared by sequential addition of the carbon donor fragments to **1**, starting with either ligand (Scheme 2). For instance, stirring of an acetone solution of **1** under 1 atm ethylene at room temperature produces the displacement of one of the coordinated solvent molecules by ethylene to afford  $[\text{OsTp}(\eta^2\text{--CH}_2\text{=CH}_2)(\kappa^1\text{--OCMe}_2)(\text{P}^i\text{Pr}_3)]\text{BF}_4$  (**4**), which reacts with phenylacetylene to give **2**. Alternatively, the addition of 1.25 equiv of phenylacetylene to an acetone solution of **1** at room temperature leads to the vinylidene derivative  $[\text{OsTp}(\text{C}=\text{CHPh})(\kappa^1\text{--OCMe}_2)(\text{P}^i\text{Pr}_3)]\text{BF}_4$  (**5**), which gives **2** under 1 atm ethylene.

#### Scheme 2



The ethylene complex **4** was isolated as a yellow solid in 87% yield. The X-ray structure proves the presence of both acetone and ethylene in the complex. The  $\text{Os--C}(1)$ ,  $\text{Os--C}(2)$ , and  $\text{C}(1)\text{--C}(2)$  distances of 2.163(4), 2.181(4), and 1.355(6) Å, respectively, compare well with those of **2**. The vinylidene derivative **5** was isolated as a brown solid in 69% yield. Its X-ray structure proves the tautomerization of the alkyne.<sup>15</sup> As in **2**, the coordination of the vinylidene is nearly linear, with an  $\text{Os--C}(1)\text{--C}(2)$  angle of 179.0(3)° and  $\text{Os--C}(1)$  and  $\text{C}(1)\text{--C}(2)$  distances of 1.834(4) and 1.315(6) Å, respectively.

In conclusion, transition-metal complexes can promote the cleavage of both  $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^2)$  bonds of alkylidene-cyclopropanes. The process is proposed to take place via metallacyclopropene intermediates stabilized by an ethylene chelation assistant. The

driving force for the fragmentation is the high stability of the resulting  $\pi$ -olefin–M–vinylidene species.

**Acknowledgment.** Financial support was provided by the Spanish MICINN [Projects CTQ2008-00810, SAF2007-61015, and Consolider Ingenio 2010 (CSD2007-00006)], Diputación General de Aragón (E35), and Xunta de Galicia (GRC2006/132). L.S. and L.V. thank MICINN and Xunta de Galicia for their grants.

**Supporting Information Available:** Experimental details regarding the synthesis; characterization data and crystallographic data (CIF) for **2**, **4**, and **5**; and details of the computational studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

#### References

- (1) (a) Murakami, M.; Ito, Y. *Top. Organomet. Chem.* **1999**, 3, 97. (b) Jun, C.-H. *Chem. Soc. Rev.* **2004**, 33, 610.
- (2) Rytchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, 38, 870.
- (3) (a) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324. (b) Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, 108, 7222.
- (4) (a) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1984**, 106, 3054. (b) Nishimura, T.; Uemura, S. *J. Am. Chem. Soc.* **1999**, 121, 11010. (c) Rytchinski, B.; Oevers, S.; Montag, M.; Vignalok, A.; Rozenberg, H.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2001**, 123, 9064. (d) Jun, C.-H.; Moon, C. W.; Lee, H.; Lee, D.-Y. *J. Mol. Catal. A: Chem.* **2002**, 189, 145. (e) Gandelman, M.; Shimom, L. J. W.; Milstein, D. *Chem.–Eur. J.* **2003**, 9, 4295.
- (5) (a) Miller, C.; Iverson, C. N.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **2001**, 123, 9718. (b) Gunay, A.; Jones, W. D. *J. Am. Chem. Soc.* **2007**, 129, 8729.
- (6) (a) Yang, X.; Jia, L.; Marks, T. J. *J. Am. Chem. Soc.* **1993**, 115, 3392. (b) Jones, W. D. *Nature* **1993**, 364, 676. (c) Yang, X.; Seyam, A. M.; Fu, P.-F.; Marks, T. J. *Macromolecules* **1994**, 27, 4625. (d) Jennings, P. W.; Johnson, L. L. *Chem. Rev.* **1994**, 94, 2241. (e) Jia, L.; Yang, X.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, 118, 1547. (f) Perthuisot, C.; Edelbach, B. L.; Zubris, D. L.; Jones, W. D. *Organometallics* **1997**, 16, 2016. (g) Wick, D. D.; Northcutt, T. O.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, 17, 4484. (h) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **1998**, 120, 2843.
- (7) (a) Tipper, C. F. H. *J. Chem. Soc.* **1955**, 2045. (b) Adams, D. M.; Chatt, J.; Guy, R. G.; Sheppard, N. *J. Chem. Soc.* **1961**, 738.
- (8) (a) Brandi, A.; Goti, A. *Chem. Rev.* **1998**, 98, 589. (b) Brandi, A.; Cicchi, S.; Cordero, F. M.; Goti, A. *Chem. Rev.* **2003**, 103, 1213.
- (9) (a) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, 96, 49. (b) Nakamura, I.; Yamamoto, Y. *Adv. Synth. Catal.* **2002**, 344, 111. (c) Delgado, A.; Rodríguez, J. R.; Castedo, L.; Mascareñas, J. L. *J. Am. Chem. Soc.* **2003**, 125, 9282. (d) Gullías, M.; García, R.; Delgado, A.; Castedo, L.; Mascareñas, J. L. *J. Am. Chem. Soc.* **2006**, 128, 384. (e) Rubín, M.; Rubina, M.; Gevorgyan, V. *Chem. Rev.* **2007**, 107, 3117. (f) Gullías, M.; Durán, J.; López, F.; Castedo, L.; Mascareñas, J. L. *J. Am. Chem. Soc.* **2007**, 129, 11026. (g) Aïssa, C.; Fürstner, A. *J. Am. Chem. Soc.* **2007**, 129, 14836. (h) García-Fandiño, R.; Gullías, M.; Castedo, L.; Granja, J. R.; Mascareñas, J. L.; Cárdenas, D. J. *Chem.–Eur. J.* **2008**, 14, 272. (i) Masarwa, A.; Fürstner, A.; Marek, I. *Chem. Commun.* **2009**, 5760. (j) Villarino, L.; López, F.; Castedo, L.; Mascareñas, J. L. *Chem.–Eur. J.* **2009**, 15, 13308.
- (10) (a) Mashima, K.; Takaya, H. *Organometallics* **1985**, 4, 1464. (b) Tantillo, D. J.; Carpenter, B. K.; Hoffmann, R. *Organometallics* **2001**, 20, 4562. (c) Binger, P.; Müller, P.; Podubrin, S.; Albus, S.; Krüger, C. *J. Organomet. Chem.* **2002**, 656, 288. (d) Nishihara, Y.; Yoda, C.; Itazaki, M.; Osakada, K. *Bull. Chem. Soc. Jpn.* **2005**, 78, 1469. (e) Kozhushkov, S. I.; Fürstner, J.; Kakoschke, A.; Stellfeldt, D.; Yong, L.; Wartchow, R.; de Meijere, A.; Butenschön, H. *Chem.–Eur. J.* **2006**, 12, 5642.
- (11) Castro-Rodrigo, R.; Esteruelas, M. A.; Fuertes, S.; López, A. M.; López, F.; Mascareñas, J. L.; Mozo, S.; Oñate, E.; Saya, L.; Villarino, L. *J. Am. Chem. Soc.* **2009**, 131, 15572.
- (12) (a) Huang, D. J.; Oliván, M.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, 17, 4700. (b) Esteruelas, M. A.; Oliván, M.; Oñate, E.; Ruiz, N.; Tajada, M. A. *Organometallics* **1999**, 18, 2953. (c) Baya, M.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2005**, 24, 2030.
- (13) (a) Johnson, T. J.; Albinati, A.; Koetzle, T. F.; Ricci, J.; Eisenstein, O.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1994**, 33, 4966. (b) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E. *Organometallics* **2000**, 19, 3260.
- (14) (a) Buil, M. L.; Eisenstein, O.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M.; Oñate, E.; Ruiz, N.; Tajada, M. A. *Organometallics* **1999**, 18, 4949. (b) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2003**, 22, 2472.
- (15) (a) Bruce, M. I. *Chem. Rev.* **1991**, 91, 197. (b) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, 193–195, 977. (c) Esteruelas, M. A.; López, A. M. *Organometallics* **2005**, 24, 3584. (d) Esteruelas, M. A.; López, A. M.; Oliván, M. *Coord. Chem. Rev.* **2007**, 251, 795.

JA909240Q