Organometallics **2006,** *25,* 6162−6165

A Five-Center Rather than a Four-Center Transition State for Alkene Insertion into the Metal−Alkyl Bond of a Cationic Binuclear Yttrium Complex

Yi Luo and Zhaomin Hou*

Organometallic Chemistry Laboratory, RIKEN (The Institute of Physical and Chemical Research), Hirosawa 2-1, Wako, Saitama 351-0198, Japan, and PRESTO, Japan Science and Technology Agency (JST), Saitama 332-0012, Japan

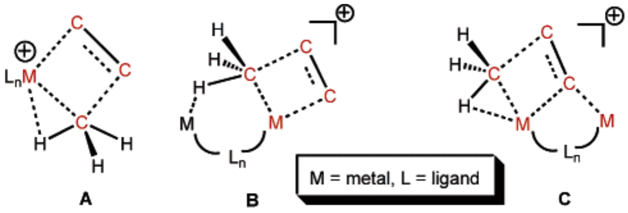
Received August 3, 2006

Summary: The insertion reactions of isoprene and ethylene into the Y−CH_2SiH_3 bond of a cationic binuclear yttrium complex are computationally investigated by use of the hybrid B3LYP density functional method. It has been found that these insertion reactions take place via a kinetically preferable five-center transition state rather than a conventional four-center transition state that is well known for the mononuclear-complex-catalyzed alkene insertion reactions. The cooperative bonding of the two metal centers to an alkene moiety plays an important role for the stabilization of the five-center transition state in the present system.

Introduction

The insertion of an alkene into the metal−alkyl (M−R) bond of a cationic metal alkyl species is an important approach to the formation of a C−C bond.[1] Detailed knowledge of the reaction mechanism is crucial for a useful understanding of such a process and development of new catalysts. It has been widely accepted for a long time that this insertion process follows a general (α-agostic interaction assisted) four-center transition state (TS) mechanism,[2] in which the olefin initially approaches the metal center to form a π-complex and then the reaction proceeds via a four-center TS (such as **A** in Chart 1), leading to the insertion product. Such a mechanism has been experimentally confirmed[3] and also computationally modeled[1c,4,5] for mononuclear-complex-catalyzed alkene insertion reactions. Speculatively, if such a reaction is catalyzed by a binuclear metal complex, there are two possibilities for the insertion TS. One is the four-center TS involving a single metal atom (such as **B** in Chart 1), and the other is a five-center TS involving two cooperative metal atoms (such as **C** in Chart 1). However, to the best of our knowledge, theoretical investigation of the latter has not been reported previously, although binuclear metal complexes have received much recent attention because of their intermetallic cooperative reactivity.[6] We have recently reported a cationic binuclear yttrium alkyl species, **1** (Chart 2), showing unprecedented isospecific 3,4-selectivity in the polymerization of isoprene.[7] In the study of the reaction mechanism of such a binuclear system, we found that the insertion of isoprene (C_5H_8) or ethylene (C_2H_4) into the Y−CH_2SiH_3 bond of **2**, a computational model compound of **1** (Chart 2),[8] proceeds via a five-center rather than a four-center TS. We report here these results, which may shed new light on the reaction mechanism of alkene insertion into the M−R bond.

Chart 1. Transition States for Alkene Insertion into M−R Bonds



---

* Corresponding author. Fax: (81) 48-462-4665. E-mail: houz@riken.jp.

[1] For examples of reviews, see: (a) Widenhoefer, R. A. *Acc. Chem. Res.* **2002**, *35*, 905−913. (b) Chen, E. Y. X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391−1434. (c) Koga, N.; Morokuma, K. *Chem. Rev.* **1991**, *91*, 823−842. (d) Okuda, J.; Arndt, S.; Beckerle, K.; Hultzsch, K. C.; Voth, P.; Spaniol, T. P. In *Organometallic Catalysts and Olefin Polymerization*; Blom, R., Eds.; Springer-Verlag: Berlin, Germany, 2001; pp 156−165. (e) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236−2257. (f) Erker, G. *Acc. Chem. Res.* **2001**, *34*, 309−317. (g) Corradini, P.; Guerra, G.; Cavallo, L. *Acc. Chem. Res.* **2004**, *37*, 231−241. (h) Angermund, K.; Fink, G.; Jensen, V. R.; Kleinschmidt, R. *Chem. Rev.* **2000**, *100*, 1457−1470. (i) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253−1346. (j) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663−682. (k) Hou, Z. *J. Synth. Org. Chem., Jpn.* **2005**, *63*, 1124−1136. (l) Hou, Z.; Luo, Y.; Li, X. *J. Organomet. Chem.* **2006**, *691*, 3114−3121. (m) Zeimentz, P. M.; Arndt, S.; Elvidge, B. R.; Okuda, J. *Chem. Rev.* **2006**, *106*, 2404−2433.

[2] (a) Cossée, P. *J. Catal.* **1964**, *3*, 80−88. (b) Arlman, E. J. *J. Catal.* **1964**, *3*, 89−98. (c) Arlman, E. J.; Cossée, P. *J. Catal.* **1964**, *3*, 99−104. (d) Brookhart, M.; Green, M. L.H. *J. Organomet. Chem.* **1983**, *250*, 395−408. (e) Grubbs, R.; Coates, G. W. *Acc. Chem. Res.* **1996**, *29*, 85−93.

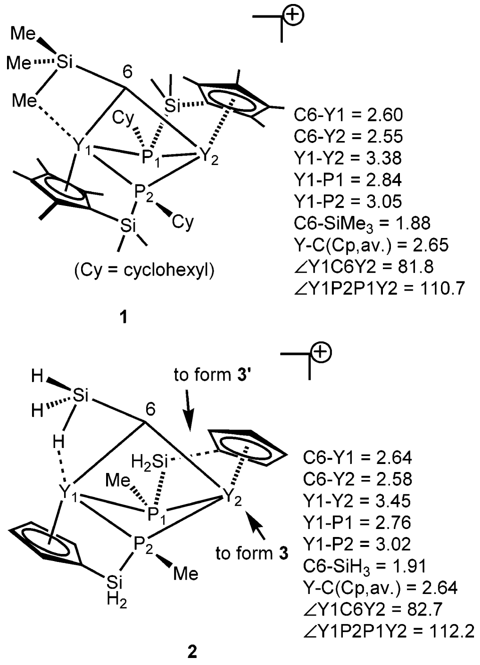
[3] (a) Clawson, L.; Soto, J.; Buchwald, S. L.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 3377−3378. (b) LeClerc, M. K.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1995**, *117*, 1651−1652. (c) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566−1577. (d) Krauledat, H.; Brintzinger, H. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1412−1413.

[4] For reviews, see: (a) Rappe, A. K.; Skiff, W. M.; Casewit, C. J. *Chem. Rev.* **2000**, *100*, 1435−1456. (b) Niu, S.; Hall, M. B. *Chem. Rev.* **2000**, *100*, 353−406. (c) Michalak, A.; Ziegler, T. In *Computational Modelling of Homogeneous Catalysis, Volume 25*; Feliu, M., Agusti L., Eds.; Kluwer: Dordrecht, 2002; pp 57−78. (d) Tobisch, S. *Acc. Chem. Res.* **2002**, 35, 96−104.

[5] For examples, see: (a) Woo, T. K.; Ziegler, T. *Organometallics* **1994**, *13*, 2252−2261. (b) Xu, Z.; Vanka, K.; Firman, T.; Michalak, A.; Zurek, E.; Zhu, C.; Ziegler, T. *Organometallics* **2002**, *21*, 2444−2453. (c) Flisak, Z.; Ziegler, T. *Macromolecules* **2005**, *38*, 9865−9872. (d) Margl, P.; Deng, L.; Ziegler, T. *J. Am. Chem. Soc.* **1998**, *120*, 5517−5525. (e) Froese, R. D. J.; Musaev, D. G.; Morokuma, K. *Organometallics* **1999**, *18*, 373−379. (f) Froese, R. D. J.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1998**, *120*, 1581−1587. (g) Froese, R. D. J.; Musaev, D. G.; Matsubara, T.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 7190−7196. (h) Musaev, D. G.; Froese, R. D. J.; Svensson, M.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 367−374. (i) Froese, R. D. J.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1998**, *120*, 1581−1587. (j) Yoshida, T.; Koga, N.; Morokuma, K. *Organometallics* **1996**, *15*, 766−777. (k) Margl, P.; Deng, L.; Ziegler, T. *Organometallics* **1998**, *17*, 933−946. (l) Deng, L.; Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 1094−1100. (m) Tobisch, S.; Bogel, H.; Taube, R. *Organometallics* **1998**, *17*, 1177−1196. (n) Tobisch, S. *J. Am. Chem. Soc.* **2004**, *126*, 259−272. (o) Lanza, G.; Fragala, I. L.; Marks, T. J. *Organometallics* **2001**, *20*, 4006−4017. (p) Lanza, G.; Fragala, I. L.; Marks, T. J. *Organometallics* **2002**, *21*, 5594−5612.

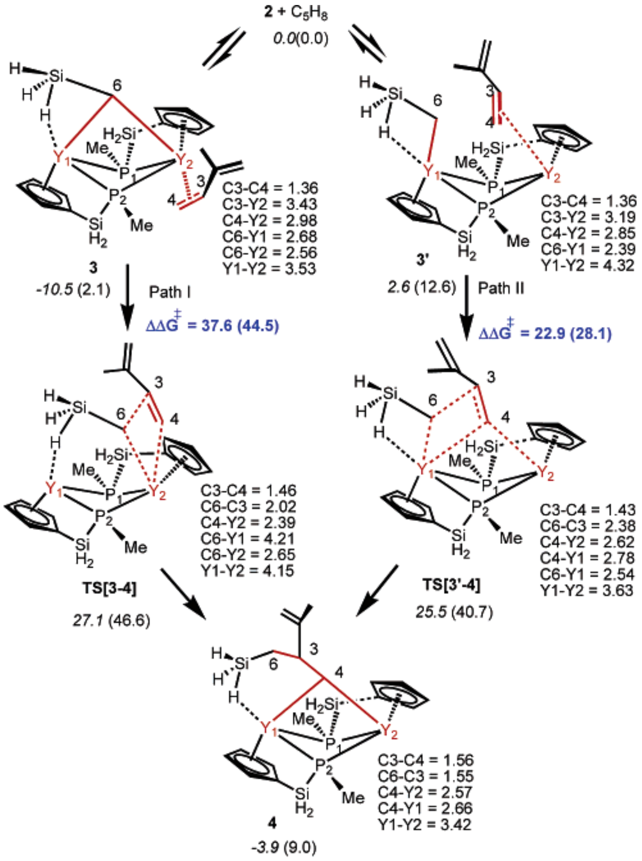
10.1021/om060702i CCC: $33.50

Chart 2. Cationic Binuclear Yttrium Alkyl Species 1 and Its Model Compound 2 (bond lengths in Å and angles in deg; arrows in 2 showing the approach direction of an alkene)



Results and Discussion

Scheme 1. Stationary Points (bond length in Å) for Isoprene Insertion along a Four-Center TS Pathway (Path I) and a Five-Center TS Pathway (Path II) Together with the Relative Gibbs Free Energy (kcal/mol) in Solution (italics) and Gas Phase (in parentheses)



The insertion reaction of C_5H_8[9] begins with its approach to the sterically open Y2 center of **2** rather than the crowded Y1 center because of the agostic interaction between Y1 and the SiH_3 group (Chart 2). The access of C_5H_8 from the right side of Y2 leads to the π-complex **3**, retaining the H_3SiCH_2-bridging feature, which then undergoes a four-center (C6, C3, C4, and Y2) TS, **TS[3-4]**, with the breakage of the Y1−C6 bond, and leads to the insertion product **4** with a restoration of the alkyl-bridging feature (Path I in Scheme 1). However, the rather high free-energy barrier (e.g., 37.6 kcal/mol in chlorobenzene) for the conversion of **3** to **4** is almost kinetically inaccessible and may restrain the reaction from following Path I (Scheme 1).[10] This led us to wonder whether there is a kinetically feasible alternative pathway.

By an access of C_5H_8 from the upside of Y2,[11] the π-complex **3′** is formed. In this process, the C6−Y2 bond is broken and the dihedral angle ∠Y1P1P2−P1P2Y2 increases from 113° in **2** to 149° in **3′**. The reaction then proceeds via a five-center TS, **TS[3′-4]**, by overcoming a solvation free-energy barrier of 22.9 kcal/mol, to yield the identical insertion product **4** (Path II, Scheme 1). Essentially, the bridging CH_2SiH_3 group in **2** plays the role of an electron-mediating "buffer" facilitating the upside coordination of the incoming isoprene to the Y2 atom and its insertion process. In this sense, the strength of a carbon−metal bond, such as C6−Y2, could be a possible factor affecting the formation of the π-complex (such as **3′**) and hence the catalytic activity. Although the breakage of the C6−Y2 bond makes the formation of **3′** slightly endoergic (Scheme 1), the lower free-energy barrier (22.9 kcal/mol), compared with that along Path I (37.6 kcal/mol), allows the insertion reaction to occur smoothly.[12,13] The IRC calculation and further releases (optimization to minimum) confirmed that **TS[3′-4]** exactly connects **3′** and **4** on the potential energy surface. In **TS[3′-4]**,

---

(6) For examples, see: (a) Li, H.; Li, L.; Marks, T. J.; Sands, L. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 10788−1789. (b) Abramo, G. P.; Li, L.; Marks, T. J. *J. Am. Chem. Soc.* **2002**, *124*, 13966−13967. (c) Keaton, R. J.; Sita, L. R. *J. Am. Chem. Soc.* **2001**, *123*, 10754−1755. (d) Utko, J.; Przybylak, S.; Jerzykiewicz, L. B.; Szafert, S.; Sobota, P. *Chem. Eur. J.* **2003**, *9*, 181−190. (e) Keaton, R. J.; Jayaratne, K. C.; Fettinger, J. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 12909−12910. (f) Li, H.; Li, L.; Schwartz, D. J.; Metz, M. V.; Marks, T. J.; Liable-Sands, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **2005**, *127*, 14756−1768. (g) Li, H.; Stern, C. L.; Marks, T. J. *Macromolecules* **2005**, *38*, 9015−9027. (h) Khoroshun, D. V.; Inagaki, A.; Suzuki, H.; Vyboishchikov, S. F.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **2003**, *125*, 9910−9911. (i) Baar, C. R.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2001**, *20*, 3459−3465. (j) Bigot, B.; Delbecq, F. *Organometallics* **1987**, *6*, 172−180. (k) Delbecq, F. *Organometallics* **1990**, *9*, 2223−2233.

(7) Zhang, L.; Luo, Y.; Hou, Z. *J. Am. Chem. Soc.* **2005**, *127*, 14562−14563.

(8) The structure **1** was obtained by static and dynamic computations based on the X-ray structure of its neutral complex precursor $[Me_2Si(C_5Me_4)(\mu\text{-}PCy)YCH_2SiMe_3]_2$ and was confirmed to be a true active species for the polymerization of isoprene. See ref 7 for more details.

(9) The data for isoprene insertion given here are for 4,3-insertion in the methyl-*exo* fashion. Isoprene 4,3-insertion in the methyl-*endo* fashion also prefers a five-center TS pathway (see Supporting Information for more details). Because the 3,4-polyisoprene has been experimentally obtained in very high regioselectivity, the 1,4-insertion fashion was not considered in this work. An attempt to model the 3,4-insertion process finally led to the 1,4-insertion product, which was therefore not considered further. The coordination in a *cis*-fashion will not alter the reaction pathway.

(10) The slightly large variation trend in solvation energy may result from the fairly high polarity of the chlorobenzene solvent and the significant geometrical variation of the stationary points.

(11) The $H_2SiC_5H_4$ and (P2)Me groups sterically inhibit the access of isoprene to Y2 from either the back-side or front-side.

(12) An attempt to locate a transition state to connect **3** and **3′** was not successful. The reactants **2** and isoprene could be viewed to be in equilibrium with the π-complexes **3** and **3′** (Scheme 1).

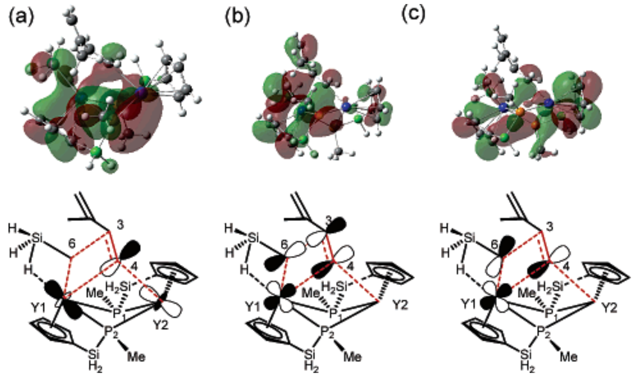


Figure 1. Orbital isosurfaces of the five-center TS **TS[3′-4]** for isoprene insertion. (a) HOMO (MO = 91a); (b) HOMO-2 (MO = 89a); (c) HOMO-5 (MO = 86a). Schematic representations for the atomic orbital overlaps among the five atoms (Y1, C6, C3, C4, and Y2) are shown below the molecular orbital isosurfaces.

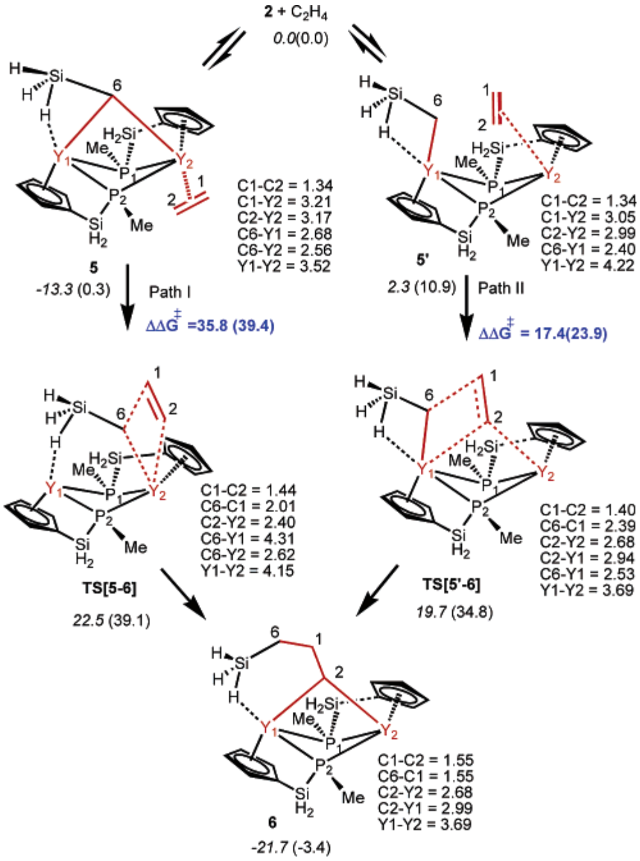
the Y1, C6, C3, C4, and Y2 atoms form a coplanar cyclic five-center structure with an average deviation of 0.04 Å from the least-squares plane formed by the five atoms (Scheme 1). The isoprene moiety interacts not only with C6 and Y1 (C6···C3 distance of 2.38 Å and C4···Y1 contact of 2.78 Å) but also with Y2 (C4···Y2 distance of 2.62 Å). This cooperative bonding of the two metal atoms to the isoprene moiety plays an important role for the stabilization of the five-center **TS[3′-4]**, which is not observed in a conventional four-center TS structure such as **TS[3-4]** (Scheme 1). An agostic interaction between Y1 and H(SiH_2) is also observed in the five-center **TS[3′-4]**, as in the case of the four-center **TS[3-4]**.

The orbital interactions corroborating the cyclic five-center TS structure can be seen from the isosurfaces of molecular orbitals. For example, the HOMO (highest occupied molecular orbital) shows interactions between the 2p orbitals of C4 and the 4d orbitals of the two Y atoms (Figure 1a). The HOMO-5 and HOMO-2 demonstrate the orbital overlaps among the C6, C4, and Y1 atoms and those among the C6, C3, C4, and Y1 atoms, respectively (Figure 1b,c). These geometrical features and chemical bondings strongly support the cyclic five-center structure of **TS[3′-4**].

In agreement with the experimental result,[7] the Lu analogue of **2** was computed to be less active than **2** since the Lu analogue induced higher complexation energy (10.7 kcal/mol) and insertion free-energy barrier (25.9 kcal/mol, see Supporting Information for more details) compared with **2** (2.6 and 22.9 kcal/mol, respectively).

To see whether the five-center TS pathway is available for other alkenes, we investigated the insertion of ethylene into the Y2−CH_2SiH_3 bond of **2**. The geometries and the relative free energies of stationary points along the four-center TS and five-center TS pathways are shown in Scheme 2. It can be seen that the geometrical features of the stationary points are similar to those for isoprene insertion. As expected, the free-energy barrier along the five-center TS pathway (17.4 kcal/mol) is significantly lower than that along the four-center TS pathway (35.8 kcal/mol). Therefore, it can be concluded that the insertions of both isoprene and ethylene into the metal−alkyl bond of the cationic binuclear yttrium alkyl species **2** proceed via a significantly favorable five-center transition state rather than a conventional four-center transition state. A study on the insertion reaction of alkenes into the M−R(H) bonds of other bi- or polynuclear complexes is in progress.

Scheme 2. Stationary Points (bond length in Å) for Ethylene Insertion along a Four-Center TS Pathway (Path I) and a Five-Center TS Pathway (Path II) Together with the Relative Gibbs Free Energy (kcal/mol) in Solution (italics) and Gas Phase (in parentheses)



Computatonal Details

The geometry optimizations and energy estimations were carried out with the method of the hybrid B3LYP density functional.[14] This method has been successfully applied for many organometallic systems.[15,16] The 6-31G* basis set was considered for the C and H atoms. The Stuttgart/Dresden effective core potentials as well as the optimized valence basis sets,[17] (4s4p)/[2s2p], (4s4p)/[2s2p], and (8s7p6d)/[6s5p3d], were used for Si, P, and Y, respectively (called SDD in the Gaussian program). Moreover, a polarized f-function for Y atoms (exponent of 0.84) and d-functions for Si (exponent

---

(13) The lower stability (higher energy) of **4** than that of **3** might suggest that **4** is a highly reactive intermediate, which could subsequently undergo an energetically favorable isoprene insertion/polymerization reaction. Such situations have been observed previously in other systems (e.g., Blok, A. N.; Budzelaar, P. H. M.; Gal, A. W. *Organometallics* **2003**, *22*, 2564−2570). However, further calculations on the reactions taking place at **4** are difficult because of the hugeness of the computational resources required for such a large system.

(14) (a) Beck, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(15) (a) Silanes, I.; Mercero, J. M.; Ugalde, J. M. *Organometallics* **2006**, *25*, 4483−4490. (b) Sassmannshausen, J.; Green, J. C.; Stelzer, F.; Baumgartner, J. *Organometallics* **2006**, *25*, 2796−2805. (c) Silanes, I.; Ugalde, J. M. *Organometallics* **2005**, *24*, 3233−3246. (d) Bobadova-Parvanova, P.; Wang, Q.; Quinonero-Santiago, D.; Morokuma, K.; Musaev, D. G. *J. Am. Chem. Soc.* **2006**, *128*, 11391−11403.

(16) Although the second-order perturbative method MP2 (cf. Head-Gordon, M.; Head-Gordon, T. *Chem. Phys. Lett.* **1994**, *220*, 122−128) could be more accurate, it is difficult to use this method in the present bimetallic system, because it requires much huger computational resources.

(17) (a) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123−141. (b) Bergner, A.; Dolg, M.; Kuechle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431−1441.

of 0.45) and P (exponent of 0.55) were augmented, respectively, for more accurate computational results.[18] The stability of the wavefunction was tested to be stable for each case. Normal coordinate analysis was performed for the conformation of all stationary points and thermodynamic data. Chlorobenzene[7] solvation energy calculations were carried out on the basis of the gas-phase-optimized geometries by use of the CPCM model.[19,20] The ion-pairing effect was not considered due to huge computational consumption. In fact, the anion−cation interaction should be very weak in the present system, because of the weak coordination power of the anion unit $B(C_6F_5)_4^-$ and the bulkiness of the ligands in the cationic part.[1b,21] A C_1 symmetry point group was used throughout all calculations, and no higher molecular symmetry restriction was imposed. All calculations were performed utilizing the Gaussian 03 program.[22]

Acknowledgment. This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 14078224, “Reaction Control of Dynamic Complexes”) (to Z.H.) and for Young Scientists (No. 17750061) (to Y.L.) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. We thank the RIKEN Super Combined Cluster (RSCC) for computational resources.

Supporting Information Available: Full citation of ref 21, figures and tables giving the structure and relative free energy for isoprene insertion in the methyl-*endo* fashion, IRC following of **TS[3′-4]**, optimized Cartesian coordinates and energies together with imaginary frequencies of TSs, and structures and energy data for the analogous Lu-assisted isoprene insertions. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060702I

---

(18) (a) Suresh, C. H.; Koga, N. *Organometallics* **2001**, *20*, 4333−4344. (b) Ehlers, A. W.; Boehme, M.; Dapprich, S.; Gobbi, A.; Hoellwarth, A.; Jonas, V.; Koehler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111−14. (c) Perrin, L.; Maron, L.; Eisenstein, O. *Faraday Discuss.* **2003**, *124*, 25−39.

(19) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995−2001.

(20) The CPCM model has been widely used for the investigation of the solvation effect in various metal complex systems. For examples, see: (a) Vallet, V.; Wahlgren, U.; Grenthe, I. *J. Am. Chem. Soc.* **2003**, *125*, 14941−14950. (b) Clot, E.; Eisenstein, O.; Weng, T.-C.; Penner-Hahn, J.; Caulton, K. G. *J. Am. Chem. Soc.* **2004**, *126*, 9079−9084. (c) Holscher, M.; Keul, H.; Hocker, H. *Macromolecules* **2002**, *35*, 8194−8202.

(21) (a) Harney, M. B.; Keaton, R. J.; Fettinger, J. C.; Sita, L. R. *J. Am. Chem. Soc.* **2006**, *128*, 3420−3432. (b) Recent computations for group 4 catalyst: Talarico, G.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **2006**, *128*, 4524−4525.

(22) Frisch, M. J.; et al. *Gaussian 03*, Revision C.01; Gaussian, Inc.: Wallingford, CT, 2004. See Supporting Information for full citation.