

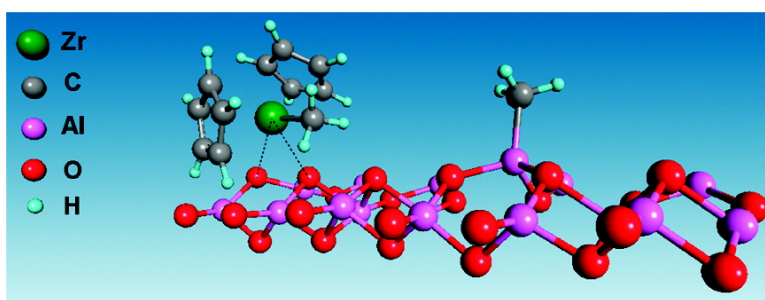
Article

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Alessandro Motta, Ignazio L. Fragala#, and Tobin J. Marks

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## Links Between Single-Site Heterogeneous and Homogeneous Catalysis. DFT Analysis of Pathways for Organozirconium Catalyst Chemisorptive Activation and Olefin Polymerization on $\gamma$ -Alumina

Alessandro Motta,<sup>†</sup> Ignazio L. Fragalà,<sup>\*,†</sup> and Tobin J. Marks<sup>\*,‡</sup>

*Dipartimento di Scienze Chimiche, Università di Catania, and INSTM, UdR Catania, Viale A. Doria 6, 95125 Catania, Italy, and Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113*

Received April 3, 2008; E-mail: lfragala@dipchi.unict.it; t-marks@northwestern.edu

**Abstract:** This contribution focuses on the catalytic properties of the organozirconium precatalyst  $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$  chemisorbed on dehydroxylated  $\gamma$ -alumina ( $\text{Al}_2\text{O}_3$ ), as analyzed via density functional theory. The interactions of the catalytically active cationic  $\text{Cp}_2\text{ZrCH}_3^+$  adsorbate species are scrutinized at two possible model  $\text{Al}_2\text{O}_3$  (110) surface sites, namely  $\mu_2$ -O and  $\mu_3$ -O, representing the principal reactive species on the alumina surface. It is found that zirconocenium coordination occurs via two different geometries (dioxo-bridged and oxo-bridged) at both the  $\mu_3$ -O and  $\mu_2$ -O surface sites. This process is compared to that for forming the related homogeneous phase  $\text{Cp}_2\text{ZrCH}_3^+\text{H}_3\text{CB}(\text{C}_6\text{F}_5)_3^-$  ion pair structure. It is found that the interaction of the  $\text{Cp}_2\text{ZrCH}_3^+$  adsorbate species with the  $\mu_2$ -O sites is far stronger than that with the  $\mu_3$ -O sites due to the greater unsaturation of the former. Furthermore, the interaction with the  $\mu_3$ -O sites is weaker than that in the parent homogeneous ion pair. The catalytic activity of the chemisorbed  $\text{Cp}_2\text{ZrCH}_3^+$  systems for ethylene polymerization is investigated at both  $\mu_2$ -O and  $\mu_3$ -O sites and compared with the analogous  $\text{Cp}_2\text{ZrCH}_3^+\text{H}_3\text{CB}(\text{C}_6\text{F}_5)_3^-$ -mediated process in solution. A Cossee enchainment mechanism proceeds via ethylene  $\pi$ -complex formation and an  $\alpha$ -agostic assisted transition state to yield  $\gamma$ - and  $\beta$ -agostic insertion products. The overall kinetics of enchainment are closely correlated with the energetics of  $\pi$ -complex formation, and it is suggested that the differing kinetic behaviors of the surface-bound  $\text{Cp}_2\text{ZrR}^+$  species on the various  $\text{Al}_2\text{O}_3$  coordination sites and the analogous homogeneous species reflect differences in the olefin  $\pi$ -complex stabilization energies. These computational results agree well with the experimental data which indicate that only fractions of the surface bound species are catalytically significant but that these are far more catalytically active than the homogeneous analogues.

### Introduction

Today, catalytic processes provide a wide range of essential products, from fuels and fertilizers to plastics and pharmaceuticals, and the development of enabling catalytic technologies parallels the continuously growing demands of new applications. Therefore, understanding structure–reactivity relationships in catalytic systems remains central to optimizing selectivity–activity relationships for these technologies. Indeed, the possibility of tuning these relationships explains the great attraction of homogeneous catalysts since they offer the possibility of precise, molecule-level structural control, hence systematic, iterative catalyst design for activity and/or selectivity. In this regard, group 4 metallocene olefin polymerization catalysts can exhibit high activities and precise control over product macromolecular architecture and have stimulated intense basic and applied research efforts worldwide.<sup>1</sup> The versatility of metallocene ligation enables a large variety of structures offering diverse symmetries, activities, and enchainment/stereocontrol mechanisms.

Heterogeneous catalysts of course offer many contrasting attractions, such as extraordinary degrees of coordinative unsaturation, high reactivity, and thermal robustness, as well as ease of the handling, separation, and recycling. Nevertheless, understanding structure/reactivity/selectivity relationships in heterogeneous catalysis is complicated by uncertainties in active site structure(s) and in the percentages of surface structures which are catalytically significant. For all these reasons, the past two decades have witnessed significant progress in transferring homogeneous mo-

- (1) For recent reviews, see: (a) Amin, S. B.; Marks, T. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 2006–2025. (b) Marks, T. J., Ed. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15288–15354, and contributions therein (special feature on polymerization). (c) Suzuki, N. *Top. Organomet. Chem.* **2005**, *8*, 177–216. (d) Alt, H. G. *Dalton Trans.* **2005**, *20*, 3271–3276. (e) Kaminsky, W. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 3911–3921. Wang, W.; Wang, L. *J. Polym. Mater.* **2003**, *20*, 1–8. (f) Delacroix, O.; Gladysz, J. A. *Chem. Commun.* **2003**, *6*, 665–675. (g) Kaminsky, W.; Arndt-Rosenau, M. *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed.; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2002. (h) Lin, S.; Waymouth, R. M. *Acc. Chem. Res.* **2002**, *35*, 765–773. (i) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391–1434. (j) Gladysz, J. A. *Chem. Rev.* **2000**, *100*, 1167–1168 and contributions therein. (k) Schweier, G.; Brintzinger, H.-H. *Macromol. Symp.* **2001**, *173*, 89–103. (l) Kaminsky, W. *Catal. Today* **2000**, *62*, 23–34. (m) Kaminsky, W. *Adv. Catal.* **2001**, *46*, 89–159.

<sup>†</sup> Università di Catania.

<sup>‡</sup> Northwestern University.

lecular approaches to heterogeneous catalysis, leading to the development of “single-site” heterogeneous catalysis.<sup>2</sup>

In this context, analogues of well-defined homogeneous catalytic structures have been prepared for heterogeneous catalytic applications by direct grafting/chemisorption of organometallic complexes on metal oxide surfaces. Examples include highly reactive alumina-supported zirconium hydrides for the alkane hydrogenolysis,<sup>3</sup> CH<sub>3</sub>ReO<sub>3</sub><sup>4</sup> supported on Lewis acidic supports such as silica–alumina,<sup>5</sup> alumina,<sup>6</sup> niobia,<sup>7</sup> or zeolites<sup>8</sup> for olefin metathesis, silica-supported tungsten<sup>9</sup> and molybdenum complexes<sup>10</sup> for olefin and alkane metathesis,<sup>11</sup> silica-supported tantalum hydrides for propane metathesis,<sup>12</sup> and organo-groups 4 and 5 complexes on alumina,<sup>13</sup> zirconia,<sup>14</sup> and sulfated metal oxides<sup>15</sup> for hydrogenation and polymerization catalysis, as well as organo-f-element complexes on alumina for olefin hydrogenation<sup>16,17</sup> and polymerization.<sup>17</sup> In many cases, catalytic activities far exceed those achievable with the analogous metal complexes in solution. In many cases, the structural nature of the molecule-derived adsorbates has been characterized by techniques such as NMR, EPR, vibrational,

and X-ray spectroscopies, as well as by evolved product analysis, providing informative details about surface chemisorptive and catalytic chemistry. In several cases, the percentage of adsorbate sites active for the catalytic chemistry has also been accurately quantified.<sup>13–17</sup> Despite these advances, many important kinetic and mechanistic details of such heterogeneous catalytic systems remain unclear. Fascinating and significant questions concern the following: (i) the nature of the surface organometallic species created on chemisorption, including the degree to which the original ligation is preserved; (ii) the number and type of bonds established to the oxide support and the most reactive oxide surface sites for the grafting process; (iii) the adsorbate structures which maximize catalytic activity; and (iv) the curious reasons why only small percentages of sites are sometimes catalytically active, yet their activity far exceeds that of their homogeneous analogues.<sup>13–17</sup>

For all these reasons, elucidating the nature of the interaction between chemisorbed species and surfaces represents a fundamental scientific issue, especially since there is evidence that, on passing to the homogeneous phase, activated metallocenium electrophile-weakly coordinating counteranion interactions can substantially tune catalytic properties in terms of activity, product polyolefin molecular weight, branching, and tacticity. Typical cocatalysts such as methylaluminoxane (MAO) and fluoroaryl boranes/borates have been extensively investigated, both experimentally<sup>18</sup> and theoretically,<sup>19</sup> to understand how catalytic properties depend on ion pair formation/interactions originating from cocatalyst steric and electronic characteristics. In heterogeneous catalytic cases, the chemisorbed species and the oxide surface represent a very special type of “ion pair adduct”. Therefore, comparing the key aspects of the adsorbate–oxide surface interaction with those in well-characterized solution-phase ion-pair analogues presents an attractive opportunity,

- (2) (a) Thomas, J. M.; Raja, R.; Lewis, D. W. *Angew. Chem., Int. Ed.* **2005**, *44*, 6456–6482. (b) Copéret, C.; Chabanas, R.; Petroff Saint-Arroman, R.; Basset, J.-M. *Angew. Chem., Int. Ed.* **2003**, *42*, 156–181. (c) Hlatky, G. G. *Chem. Rev.* **2000**, *100*, 1347–1376. (d) Reven, L. J. *Mol. Catal.* **1994**, *86*, 447–477. (e) Ermakov, Y. I.; Zakharov, V. A.; Nesterov, G. A. *Stud. Surf. Sci. Catal.* **1986**, *25*, 181–199. (f) Zakharov, V. A.; Yermakov, Y. I. *Catal. Rev.* **1979**, *19*, 67–103.
- (3) Joubert, J.; Delbecq, F.; Thieuleux, C.; Taoufik, M.; Blanc, F.; Copéret, C.; Thivolle-Cazat, J.; Basset, J.-M.; Sautet, P. *Organometallics* **2007**, *26*, 3329–3335.
- (4) (a) Herrmann, W. A.; Kühn, F. E. *Acc. Chem. Res.* **1997**, *30*, 169–180. (b) Romao, C. C.; Kühn, F. E.; Herrmann, W. A. *Chem. Rev.* **1997**, *97*, 3197–3246. (c) Kühn, F. E.; Scherbaum, A.; Herrmann, W. A. *J. Organomet. Chem.* **2004**, *689*, 4149–4164.
- (5) (a) Herrmann, W. A.; Wagner, W.; Flessner, U. N.; Volkhardt, U.; Komber, H. *Angew. Chem., Int. Ed.* **1991**, *30*, 1636–1638. (b) Moses, A. W.; Ramsahye, N. A.; Raab, C.; Leifste, H. D.; Chattopadhyay, S.; Chmelka, B. F.; Eckert, J.; Scott, S. L. *Organometallics* **2006**, *25*, 2157–2165.
- (6) (a) Salameh, A.; Joubert, J.; Baudouin, A.; Lukens, W.; Delbecq, F.; Sautet, P.; Basset, J.-M.; Copéret, C. *Angew. Chem., Int. Ed.* **2007**, *46*, 3870–3873. (b) Rost, A. M. J.; Schneider, H.; Zoller, J. P.; Herrmann, W. A.; Kühn, F. E. *J. Organomet. Chem.* **2005**, *690*, 4712–4718.
- (7) Buffon, R.; Choplin, A.; Leconte, M.; Basset, J.-M.; Touroude, R.; Herrmann, W. A. *J. Mol. Catal.* **1992**, *72*, L7–L10.
- (8) Malek, A.; Ozin, G. *Adv. Mater.* **1995**, *7*, 160–163.
- (9) (a) Rhers, B.; Salameh, A.; Baudouin, A.; Quadrelli, E. A.; Taoufik, M.; Copéret, C.; Lefebvre, F.; Basset, J.-M.; Solans-Monfort, X.; Eisenstein, O.; Lukens, W. W.; Lopez, L. P. H.; Sinha, A.; Schrock, R. R. *Organometallics* **2006**, *25*, 3554–3557. (b) Rhers, B.; Quadrelli, E. A.; Baudouin, A.; Taoufik, M.; Copéret, C.; Lefebvre, F.; Basset, J.-M.; Fenet, B.; Sinha, A.; Schrock, R. R. *J. Organomet. Chem.* **2006**, *691*, 5448–5455.
- (10) Blanc, F.; Thivolle-Cazat, J.; Basset, J.-M.; Copéret, C.; Hock, A. S.; Tonzetich, Z. J.; Schrock, R. R. *J. Am. Chem. Soc.* **2007**, *129*, 1044–1045.
- (11) Le Roux, E.; Taoufik, M.; Copéret, C.; de Mallmann, A.; Thivolle-Cazat, J.; Basset, J.-M.; Maunders, B. M.; Sunley, G. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6755–6758.
- (12) Rataboul, F.; Copéret, C.; Lefort, L.; de Mallmann, A.; Thivolle-Cazat, J.; Basset, J.-M. *Dalton Trans.* **2007**, 923–927.
- (13) (a) Nicholas, C. P.; Ahn, H.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 4325–4331. (b) Sishita, C.; Hathorn, R. M.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 1112–1114. (c) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57–65. (d) Dahmen, K.-H.; Hedden, D.; Burwell, R. L., Jr.; Marks, T. J. *Langmuir* **1988**, *4*, 1212–1214.
- (14) (a) Ahn, H.; Nicholas, C. P.; Marks, T. J. *Organometallics* **2002**, *21*, 1788–1806. (b) Ahn, H.; Marks, T. J. *J. Am. Chem. Soc.* **2002**, *124*, 7103–7110. (c) Ahn, H.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 13533–13534.
- (15) (a) Ahn, H.; Nicholas, C. P.; Marks, T. J. *Langmuir* **2004**, *20*, 9456–9462. (b) Nicholas, C. P.; Marks, T. J. *Nano Lett.* **2004**, *4*, 1557–1559.
- (16) Toscano, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 653–659.
- (17) (a) Eisen, M. S.; Marks, T. J. *J. Mol. Catal.* **1994**, *86*, 23–50. (b) Eisen, M. S.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 10358–10368. (c) Eisen, M. S.; Marks, T. J. *Organometallics* **1992**, *11*, 3939–3941. (d) Gillespie, R. D.; Burwell, R. L., Jr.; Marks, T. J. *Langmuir* **1990**, *6*, 1465–1477. (e) Finch, W. C.; Gillespie, R. D.; Hedden, D.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 6221–6232. (f) He, M.-Y.; Xiong, G.; Toscano, P. J.; Burwell, R. L., Jr.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 641–652.
- (18) (a) Roberts, J. A. S.; Chen, M.-C.; Seyam, A. M.; Li, L.; Zuccaccia, C.; Stahl, N. G.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 12713–12733. (b) Chen, M.-C.; Roberts, J. A. S.; Seyam, A. M.; Li, L.; Zuccaccia, C.; Stahl, N. G.; Marks, T. J. *Organometallics* **2006**, *25*, 2833–2850. (c) Stahl, N. G.; Salata, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 10898–10909. (d) Chen, M. C.; Roberts, J. A.; Marks, T. J. *Organometallics* **2004**, *23*, 932–935. (e) Chen, M.-C.; Roberts, J. A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 4605–4625. (f) Zuccaccia, C.; Stahl, N. G.; Macchioni, A.; Chen, M.-C.; Roberts, J. A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 1448–1464. (g) Beswick, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 10358–10370. (h) Deck, P. A.; Beswick, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 1772–1784. (i) Jia, L.; Yang, X.-M.; Ishihara, A.; Marks, T. J. *Organometallics* **1995**, *14*, 3135–3137. (j) Jia, L.; Yang, X.-M.; Stern, C. L.; Marks, T. J. *Organometallics* **1994**, *13*, 3755–3757.
- (19) (a) Motta, A.; Fragalà, I. L.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 7327–7338. (b) Lanza, G.; Fragalà, I. L.; Marks, T. J. *Organometallics* **2002**, *21*, 5594–5612. (c) Zurek, E.; Ziegler, T. *Prog. Polym. Sci.* **2004**, *29*, 107–148. (d) Xu, Z.; Vanca, K.; Ziegler, T. *Macromol. Symp.* **2004**, *206*, 457–469. (e) Wondimagegn, T.; Xu, Z.; Vanca, K.; Ziegler, T. *Organometallics* **2004**, *23*, 3847–3852. (f) Yang, S.-Y.; Ziegler, T. *Organometallics* **2006**, *25*, 887–900. (g) Lanza, G.; Fragalà, I. L.; Marks, T. J. *Organometallics* **2001**, *20*, 4006–4017. (h) Lanza, G.; Fragalà, I. L.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 12764–12777. (i) Lanza, G.; Fragalà, I. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 8257–8258. (j) Xu, Z.; Vanca, K.; Firman, T.; Michalak, A.; Zurek, E.; Zhu, C.; Ziegler, T. *Organometallics* **2002**, *21*, 2444–2453.

never previously realized, to better understand the unique aspects of the heterogeneous catalytic behavior, to rationally develop novel heterogeneous catalytic transformations, and, hence, to develop science-based surface organometallic chemistry.

Theoretical investigations represent an attractive means to explore the properties of chemisorbed organometallic precursors on oxide surfaces. Advances in computational resources now allow modeling of extended periodic systems, such as surfaces, and hence provide new tools to investigate organometallic surface chemistry and catalysis. In particular, surface morphologies, temperatures, and hydration levels can be theoretically modeled under realistic catalytic conditions,<sup>20</sup> thereby providing new information on catalytic site properties. Moreover, trends in heterogeneous catalytic reactivity can be correlated with precursor molecular structural and electronic factors.<sup>20,21</sup> Calculations on hybrid catalysts involving organometallic precursors and alumina surfaces have also been recently reported,<sup>4,7a,22</sup> and an informative picture of the metal complex–surface interaction is emerging. Nevertheless, catalytic mechanisms involving the chemisorbed species, their connections to homogeneous processes, and, ultimately, the differing activities of the various surface-bound active sites remain incompletely defined.

The present contribution focuses on the chemisorptive generation of a prototypical single-site heterogeneous catalyst from an archetypical group 4 metallocene,  $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ), and dehydroxylated  $\gamma$ -alumina (DA) surfaces, and on those local structural factors governing catalytic pathway(s) for ethylene polymerization. The alumina substrate exhibits pronounced Lewis acid character (due to coordinatively unsaturated surface Al sites)<sup>13,23</sup> that is phenomenologically reminiscent of analogous cocatalysts such as MAO and structurally well-defined boranes and borates<sup>11,13</sup> and, hence, allows direct comparison between the heterogeneous and homogeneous cases. The various interaction modes between the chemisorbed species and the surface are scrutinized and compared here with the interactions within analogous homogeneous phase ion pairs. Furthermore, the olefin insertion mechanism and its energetics are investigated for the most stable chemisorbed zirconocenium species and also compared with the analogous homogeneous processes. It will be seen that the present computational results agree well with the experimental data<sup>13–17</sup> which indicate that electrophilic metallocenium cations are formed upon chemi-

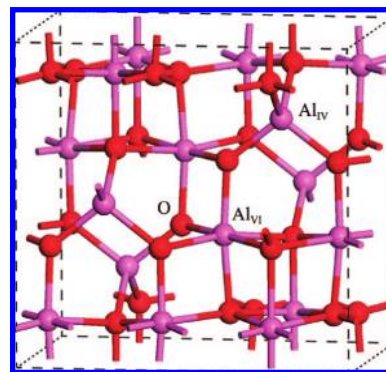


Figure 1. Optimized structure of  $\gamma$ -alumina.

sorption, that only fractions of these surface bound species are catalytically significant, but that these are far more catalytically active than their homogeneous analogues.

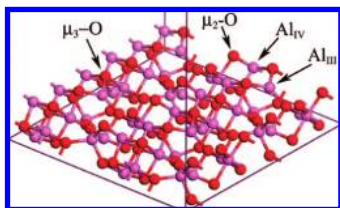
### Computational Details

All periodic DFT calculations reported here were performed using the DMol<sup>3</sup> program.<sup>24,25</sup> The electronic wave functions are expanded in atom-centered basis functions defined on a dense numerical grid. The adopted double-numeric quality basis set with polarization functions (DNP) is comparable to Gaussian 6–31\*\*, and the density functional semicore pseudo potential<sup>26</sup> (DSPP) was generated by fitting all-electron relativistic DFT results for the Zr atom. The generalized gradient-corrected (GGA) functional in the RPBE approximation<sup>27</sup> was employed. A Fermi smearing of 0.005 hartree (Ha) and a real-space cutoff of 5.2 Å were used to improve computational performance. For the numerical integration, the MEDIUM quality mesh size of the program was used. Molecular geometry optimization of stationary points used analytical gradient techniques. The “distinguished reaction coordinate procedure” was used in the analysis of the transition state geometries along the emerging C–C  $\sigma$  bond for the ethylene insertive polymerization pathways. A synchronous transit method (linear plus quadratic) was used to refine the transition state. The enthalpies ( $\Delta H$ ) reported are potential energy differences without zero point or vibrational finite temperature corrections. These terms are far too expensive to calculate for the size of the periodic systems considered here. Moreover, it was reported<sup>19j</sup> that it is expected these corrections will be on the order of 2–3 kcal/mol and, hence, represent only a slight refinement for the electronic potential energy values. Finally, it is expected that very similar corrections will apply for all the systems compared, affecting in a negligible manner the calculated trends. The charge distribution was analyzed by the Mulliken method.<sup>28</sup>

The  $\gamma$ -alumina bulk model used in this study is taken from theoretical investigations of Digne et al. and others.<sup>20b–d,29</sup> The structure (Figure 1) contains an fcc sublattice of oxide ions that generates octahedral and tetrahedral interstices which accommodate aluminum ions. In the present study, the alumina (110) surface was constructed using a slab model. It will be seen that our results for the alumina surface closely parallel those of other groups using

- (20) (a) van Santen, R. A.; Neurock, M. *Molecular Heterogeneous Catalysis. A Conceptual and Computational Approach*; Wiley-VCH: 2006. (b) Digne, M.; Sautet, P.; Raybaud, P.; Euzen, P.; Toulhoat, H. *J. Catal.* **2002**, *211*, 1–5. (c) Digne, M.; Raybaud, P.; Sautet, P.; Guillaume, D.; Toulhoat, H. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2577–2582. (d) Corral Valero, M.; Digne, M.; Sautet, P.; Raybaud, P. *Oil Gas Sci. Technol.* **2006**, *61*, 535–545.
- (21) (a) Loffreda, D.; Delbecq, F.; Vigné, F.; Saute, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 5279–5282. (b) Valcarcel, A.; Clotet, A.; Ricart, J. M.; Delbecq, F.; Saute, P. *J. Phys. Chem. B* **2005**, *109*, 14175–14182. (c) Valero, C. M.; Raybaud, P.; Sautet, P. *J. Catal.* **2007**, *247*, 339–355.
- (22) Joulbert, J.; Delbecq, F.; Sautet, P.; Le Roux, E.; Taoufik, M.; Thieuleux, C.; Blanc, F.; Copéret, C.; Thivolle-Cazat, J.; Bassat, J.-M. *J. Am. Chem. Soc.* **2006**, *128*, 9157–9169.
- (23) (a) Guillaume, D.; Gautier, S.; Despujol, I.; Alario, F.; Beccat, P. *Catal. Lett.* **1997**, *47*, 213–218. (b) Morterra, C.; Magnacca, G. *Catal. Today* **1996**, *27*, 497–532. (c) Ealet, B.; Elyakhlouffi, M. H.; Gillet, E.; Ricci, M. *Thin Solid Film* **1994**, *250*, 92–100. (d) Saad, M.; Ivanov, V. A.; Lavalley, J. C.; Nortier, P.; Luck, F. *Appl. Catal.* **1993**, *94*, 71–83. (e) Chen, F. R.; Davis, J. G.; Fripiat, J. J. *Catal.* **1992**, *133*, 263–278. (f) Nortier, P.; Fourre, P.; Saad, M.; Saur, O.; Lavalley, J. C. *Appl. Catal.* **1990**, *61*, 141–160. (g) Kijenski, J.; Baiker, A. *Catal. Today* **1989**, *5*, 1–120. (h) Knözinger, H.; Ratnasamy, P. *Catal. Rev.-Sci. Eng.* **1978**, *17*, 31–69.

- (24) (a) Delley, B. *J. Chem. Phys.* **1990**, *92*, 508–517. (b) Delley, B. *J. Phys. Chem.* **1996**, *100*, 6107–6110. (c) Delley, B. *J. Chem. Phys.* **2000**, *113*, 7756–7764.
- (25) DMol<sup>3</sup>, Materials Studio 2.0; Accelrys Inc.: San Diego, CA.
- (26) Delley, B. *Phys. Rev. B* **2002**, *66*, 155125/1–155125/9.
- (27) Hammer, B.; Hansen, L. B.; Norskov, J. K. *Phys. Rev. B* **1999**, *59*, 7413–7421.
- (28) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833–1846.
- (29) (a) Digne, M.; Sautet, P.; Raybaud, P.; Euzen, P.; Toulhoat, H. *J. Catal.* **2004**, *226*, 54–68. (b) Krokidis, X.; Raybaud, P.; Gobichon, A.-E.; Rebours, B.; Euzen, P.; Toulhoat, H. *J. Phys. Chem. B* **2001**, *105*, 5121–5230.



**Figure 2.** Aluminum and oxide sites exposed on the optimized alumina (110) surface.

similar approaches.<sup>20b–d,29</sup> Both the surface–catalyst interaction and the zirconocene-mediated ethylene polymerization processes were modeled with a (2 × 2) surface unit cell having a slab of three reticular plane thickness (72 O atoms and 48 Al atoms). The two deeper planes were frozen to simulate the bulk description and repeated periodically with a 45 Å vacuum region between the slabs. Only one catalyst molecule was placed on one side of the slab to reduce lateral interactions.

## Results and Discussion

This section focuses first on (i) the  $\gamma$ -alumina surface model and on (ii) the chemisorptive interaction of the  $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$  precatalyst with various surface coordination sites. These results are then compared and contrasted with data for the homogeneous  $\text{Cp}_2\text{ZrCH}_3^+\text{H}_3\text{CB}(\text{C}_6\text{F}_5)_3^-$  system. Next, catalytic ethylene polymerization at the activated  $\text{Cp}_2\text{ZrCH}_3^+$  adsorbate species is studied, and the results are compared with the analogous processes at the parent homogeneous catalytic system and with experimental data.

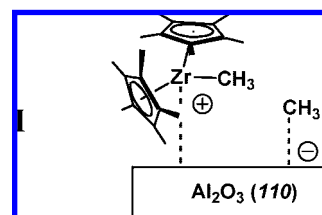
Theoretical<sup>29a</sup> and experimental<sup>13,23,30</sup> data for  $\gamma$ -alumina indicate that, in a spinel-type indexing, the (110) surface predominates, thus representing 70%–80% of the total area. The remaining area consists of (100) and (111) surfaces. Thus, the present analysis focuses on the (110) surface since it represents the principal exposed crystallographic surface. Calculations first focused on analysis of the surface sites exposed by the (110) surface. The optimized alumina (110) surface is found to exhibit significant rearrangement of Al and O ions relative to the bulk: namely bulk octahedral Al centers become pseudotetrahedral ( $\text{Al}_{\text{IV}}$  in Figure 2) while bulk tetrahedral Al centers become pseudotrigonally planar on the surface ( $\text{Al}_{\text{III}}$  in Figure 2). Therefore, the surface O ions are found to have either  $\mu_3$ -O and  $\mu_2$ -O geometries. The  $\mu_3$ -O species are bound to  $\text{Al}_{\text{III}}$  and  $\text{Al}_{\text{IV}}$  surface ions and to the octahedral  $\text{Al}_{\text{VI}}$  bulk ion, while the  $\mu_2$ -O species are bound to the  $\text{Al}_{\text{IV}}$  and to the octahedral  $\text{Al}_{\text{VI}}$  bulk ions.

Although the dehydroxylated  $\gamma$ -alumina surface (especially the 110) is not entirely dehydroxylated as shown in the literature,<sup>13,20b–d,23,29a</sup> the few remaining hydroxyl groups on the surface ( $\sim 0.1/\text{nm}^2$ )<sup>23</sup> are not considered in the present surface modeling since the coverage of the organometallic adsorbate species is far greater ( $\sim 0.25$ – $1.0/\text{nm}^2$ ).<sup>13–17</sup> Moreover, the experimental solid state  $^{13}\text{C}$  CPMAS NMR data show that the catalytic behavior of the metallocenes adsorbed on the dehydroxylated  $\gamma$ -alumina surface is overwhelmingly associated with the pronounced Lewis acid character arising from the Al sites, while any sites arising from reaction (M-alkyl protonolysis) with surface hydroxyl groups are catalytically inactive.<sup>17a,e</sup> From this perspective, the hydroxyl groups (and the related Brønsted acidity) play a negligible role in the metallocene/surface interaction and, hence, in the catalytic behavior of the heterogeneous catalytic system considered here.

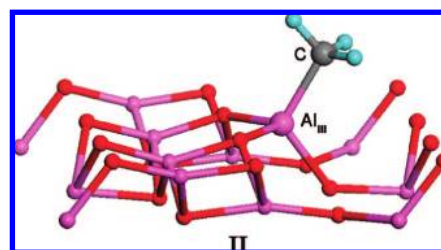
These computational results are in good agreement with previous theoretical studies<sup>29a</sup> and represent the starting point

for investigating several processes: (i) chemisorptive activation of  $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$  on the (110)  $\gamma$ -alumina surface, (ii) interaction of the resulting  $\text{Cp}_2\text{ZrCH}_3^+$  cationic species with the different surface active sites, and (iii) the catalytic sequences associated with the ethylene polymerization process.

**Characterization of Organozirconium Adsorbate Species.** The intrinsically strong Lewis acidity of the  $\gamma$ -alumina surface<sup>13,23</sup> remains primarily due to unsaturated Al ions ( $\text{Al}_{\text{III}}$  and  $\text{Al}_{\text{IV}}$  in Figure 2). These acidic sites activate the zirconocene catalyst via heterolytic Zr–C bond scission and transfer of a methide group to the surface acid sites, thus forming a “cationic” structure (I) which has been readily identified by high resolution solid state  $^{13}\text{C}$  NMR spectroscopy.<sup>13,16,17</sup>



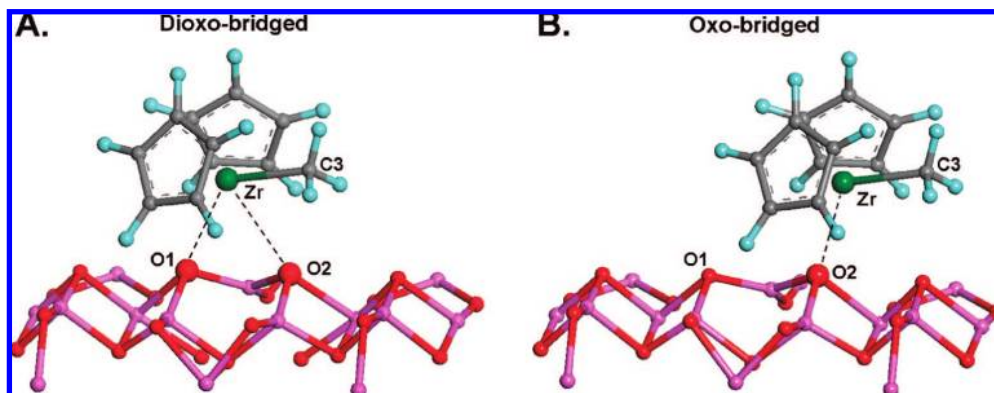
The driving force for this process lies in the unusual interaction of both the transferred methide anion and the zirconocenium cation with the surface that involves differently reactive aluminum and oxide sites (*vide supra*). The catalytic olefin activation/polymerization process, however, involves interactions associated within the surface-bound ion pair and represents the principal focus of this study. Therefore, attention is focused on the interaction of the zirconocenium cation with the alumina surface, assuming that interactions involving the transferred methide group<sup>13,17</sup> remain constant. In particular, the methide group has been placed on an aluminum pseudotrigonal planar center on the surface ( $\text{Al}_{\text{III}}$  in Figure 2) at  $\sim 5$ – $8$  Å from the metallocenium center (in agreement with solid state NMR data<sup>17</sup>). The methide interaction drastically perturbs the trigonal planar configuration of  $\text{Al}_{\text{III}}$ , as evidenced by a 0.72 Å displacement from the oxide plane (structure II). This distortion allows closer methide– $\text{Al}_{\text{III}}$  contact ( $\text{Al}_{\text{III}}$ –C = 1.97 Å), in accord with a Lewis acid–base interaction.



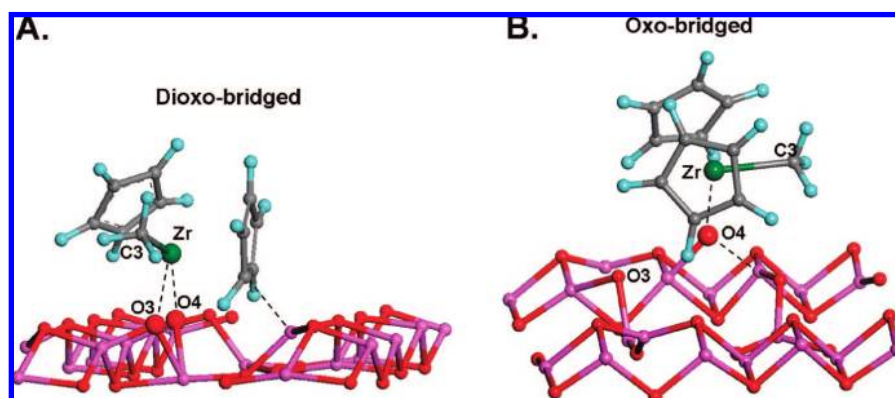
Thus, the possible ion pair interactions involving the zirconocenium cation and the alumina surface are scrutinized to search for the most stable configurations. It is found that the zirconocenium cation can undergo coordination to either  $\mu_3$ -O and  $\mu_2$ -O oxide surface species, as discussed below.

**$\mu_3$ -O Coordination.** In the case of  $\mu_3$ -O coordination, two configurations are located (Figure 3). In the first structure, the Zr atom resides between two vicinal  $\mu_3$ -O oxide ions (dioxo-bridged). The geometry of the adsorbate molecular environment is very similar to that of the precatalyst (Table 1). In particular, only minor distortions of bond lengths and bond angles between the Zr center and the coordinated cyclopentadienyl and methyl ligands are observed. The displacement angle of the Zr–C3

(30) Beaufils, J. P.; Barbaux, Y. *J. Chem. Phys.* **1981**, *78*, 347.



**Figure 3.** (A) Dioxo- and (B) oxo-bridged zirconocenium coordination on a  $\mu_3$ -O alumina surface site.



**Figure 4.** (A) Dioxo- and (B) oxo-bridged zirconocenium coordination on an alumina  $\mu_2$ -O site.

**Table 1.** Computed Geometrical Parameters (Å and deg) for the  $\text{Cp}_2\text{ZrCH}_3^+$  Catalyst Involved in Adsorbate–Alumina Surface Interactions<sup>a</sup>

	neutral precatalyst	Zr adsorbate on $\mu_3$ -O site		Zr adsorbate on $\mu_2$ -O site	
		dioxo-bridged	oxo-bridged	dioxo-bridged	oxo-bridged
Zr–Cp <sub>centr</sub>	2.28	2.26	2.27	2.33	2.28
Zr–C3	2.27	2.32	2.31	2.33	2.30
$\angle\text{Cp1–Zr–Cp2}$	133.0°	129.7°	128.4°	121.3°	128.7°
$\angle\text{Cp1–Zr–Cp2–C3}$	52.0°	67.9°	69.1°	73.8°	61.7°
Zr–Ox <sup>b</sup>		2.74	5.23	2.40	4.10
Zr–Oy <sup>b</sup>		2.90	2.58	2.28	2.13

<sup>a</sup> Labeling refers to Figures 3 and 4. <sup>b</sup> x and y are, respectively, 1 and 2 for the  $\mu_3$ -O site and 3 and 4 for the  $\mu_2$ -O site.

vector from the Cp1<sub>centr</sub>–Zr–Cp2<sub>centr</sub> plane increases and  $\angle\text{Cp1}_{\text{centr}}\text{–Zr–Cp2}_{\text{centr}}$  decreases relative to the neutral precatalyst to allow closer coordination to the surface (Table 1). The observed elongation of the Zr–C3 bond is a consequence of the surface electron density donation. The Zr metal center is not oriented symmetrically with respect to the two coordinating surface oxygen ions (Zr–O1 = 2.74 Å and Zr–O2 = 2.90 Å). This indicates a stronger O1 coordination to the Zr center (Table 1). Note also that the surface coordination of the zirconocenium ion at the  $\mu_3$ -O sites results in a sizable elongation of all proximate Al–O bonds (Table 2). Interestingly, this Al–O elongation associated with  $\mu_3$ -O1 is greater than that observed for  $\mu_3$ -O2 (Table 2), thus reflecting the greater O1 contribution to the aforementioned coordination to the electrophilic Zr center.

Another stable adsorbate configuration is located upon slight translation of the cationic Zr adsorbate species along the surface to allow coordination to a single  $\mu_3$ -O surface site (oxo-bridged configuration in Figure 3). In this case, the geometry of the activated

**Table 2.** Computed Geometrical Parameters (in Å) for the Alumina Surface Sites Involved in  $\text{Cp}_2\text{ZrCH}_3^+$  Adsorbate–Surface Binding<sup>a</sup>

	noninteracting	$\mu_3$ -O sites			
		dioxo-bridged		oxo-bridged	
		O1	O2	O1	O2
O–Al <sub>III</sub>	1.79	1.82	1.79	1.78	1.85
O–Al <sub>IV</sub>	1.84	1.87	1.85	1.84	1.92
O–Al <sub>VI</sub>	2.03	2.17	2.12	2.04	2.10
	noninteracting	$\mu_2$ -O sites			
		dioxo-bridged		oxo-bridged	
		O3	O4	O3	O4
O–Al <sub>IV</sub>	1.70	1.70	1.70	1.85	1.77
O–Al <sub>VI</sub>	1.93	2.08	2.14	1.87	3.98

<sup>a</sup> Labeling of oxygen atoms refers to Figures 3 and 4.

metallocene framework does not change relative to that in the aforementioned dioxo-bridged configuration (Table 1). However, the local surface binding geometry does reflect this altered interaction and all of the O2–Al distances are perturbed, while the O1–Al distances remain comparable to those in the noninteracting  $\gamma\text{-Al}_2\text{O}_3$  (110) sites (Table 2). Interestingly, in this oxo-bridged configuration, the computed Zr–O2 distance (2.58 Å) is shorter than the mean Zr–O distance (2.82 Å) observed in the dioxo-bridged configuration (Table 1), reflecting a significantly stronger interaction (*vide infra*).

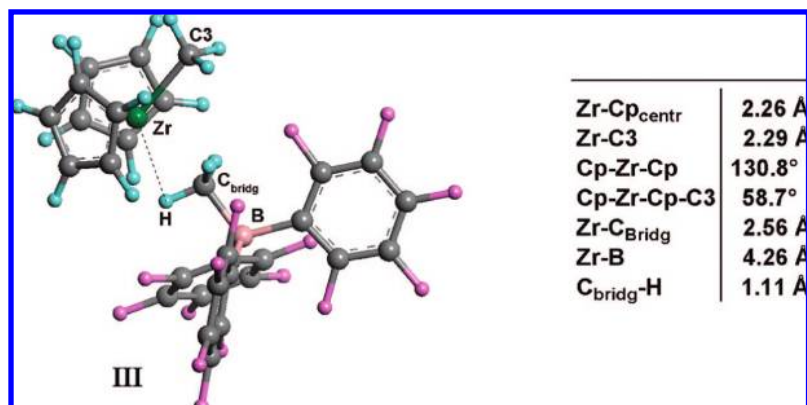
**$\mu_2$ -O Coordination.** In the case of  $\mu_2$ -O alumina surface sites, analogous dioxo- and oxo-bridged configurations are found (Figure 4). In this case, the dioxo-bridged adsorbate complex

exhibits slight distortions of the Zr–ligand bond lengths and angles versus the neutral  $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$  precatalyst. In particular, the  $\angle\text{Cp1–Zr–Cp2}$  angle decreases, and the displacement angle of the Zr– $\text{CH}_3$  vector from the Cp1–Zr–Cp2 plane increases (Table 1). These distortions are substantially greater than those in the analogous  $\mu_3\text{-O}$  dioxo-bridged configuration (Figure 3), indicating a stronger zirconocenium–surface interaction. Indeed, the Zr–O mean distance is significantly shorter ( $\Delta = -0.48$  Å) than that observed in the analogous  $\mu_3\text{-O}$  dioxo-bridged coordination (Table 1). Similar to the  $\mu_3\text{-O}$  binding environment, the Al–O bond lengths at the  $\mu_2\text{-O}$  site all increase relative to the distances in the nonproximal Al–O bonds (Table 2). Also in the case of  $\mu_2\text{-O}$  coordination, the perturbation of similar Al–O distances are not symmetrical for atoms O3 and O4. Thus, the Al–O4 distance becomes longer than that of Al–O3 as a consequence of a stronger Zr–O4 interaction (Table 2). This trend is also supported by the contracted Zr–O4 distance (2.28 Å) relative to Zr–O3 (2.40 Å). Finally, note that the chemisorptive activation of the catalyst involves significant perturbation of the  $\text{Cp}_2\text{Zr}$  framework. In fact, partial donation of some Cp electron density to the electron-deficient  $\text{Al}_{\text{III}}$  surface site is observed. This finds a counterpart in the distortion of one Cp C–H bond that is displaced from the Cp plane in  $\text{sp}^3$ -like hybridization, where the fourth coordination site is saturated by the electron-deficient  $\text{Al}_{\text{III}}$  surface site (Figure 4). Similarly, the trigonal planar configuration of  $\text{Al}_{\text{III}}$  is drastically perturbed, as evidenced by a 0.35 Å displacement from the oxide plane. These distortions allow closer Cp ligand– $\text{Al}_{\text{III}}$  contact, in accord with a Lewis acid–base interaction.

In the case of the  $\mu_2\text{-O}$  oxo-bridged configuration, surface coordination involves only the  $\mu_2\text{-O4}$  surface ion (Figure 4). Also in this case, a slight displacement of the Zr– $\text{CH}_3$  vector with respect to the Cp1–Zr–Cp2 plane and distortion of  $\angle\text{Cp1–Zr–Cp2}$  are observed relative to the precatalyst geometry; this allows more effective zirconocenium center–surface coordination. In marked contrast, the local geometry at the surface evidences substantial distortions of the O3 and O4 environments. Thus, bonding between the O4 ion and the encumbered  $\text{Al}_{\text{VI}}$  site is lost (Al–O = 3.98 Å), and a new bond is formed with a surface  $\text{Al}_{\text{IV}}$  site (O–Al = 1.94 Å; Figure 4). This concerted rearrangement brings the O4 ion between two  $\text{Al}_{\text{IV}}$  surface ions and results in closer contact with the  $\text{Cp}_2\text{ZrCH}_3^+$  center (2.13 Å) relative to the dioxo-bridged configuration (Figure 3; Table 1). The geometry in this oxo-bridged configuration shows no evidence of the ZrCp–Al surface atom Lewis acid–base interaction observed in the dioxo-bridged case (*vide supra*). Finally, bonding structures involving the zirconocenium adsorbate and both  $\mu_2\text{-O}$  and  $\mu_3\text{-O}$  donor sites are not geometrically accessible.

**Comparison to Homogeneous Zirconocenium Ion Pairs.** It is informative to compare/contrast the present heterogeneous structures bound to  $\text{Al}_2\text{O}_3$  surfaces with the parent homogeneous catalyst–cocatalyst ion pairs to better understand the similarities and differences. Therefore, the prototypical molecular  $\text{Cp}_2\text{ZrCH}_3^+\text{H}_3\text{CB}(\text{C}_6\text{F}_5)_3^-$  system was compared to the present heterogeneous systems. The homogeneous ion pair is generated by methide abstraction from  $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$  by the perfluoro-arylborane Lewis acid/cocatalyst  $\text{B}(\text{C}_6\text{F}_5)_3$ .<sup>11,18</sup> On passing from the heterogeneous to homogeneous system, a first issue concerns the possibility of different cation–counteranion orientations in the ion pairs of the latter. This possibility is not observed in the surface adsorbate species due to the rigidity of the surface compared to the molecular counteranion. Among the different orientations (Figure S1), formation of a  $\mu^3$  methyl bridging structure (computed to be the most stable) similarly induces a slight distortion of the Cp–Zr–Cp–C3 torsional angle and the  $\angle\text{Cp1–Zr–Cp2}$  angle relative to the neutral precatalyst geometry, thus allowing more effective zirconocenium–borate cocatalyst coordination (Structure III). A methyl  $\text{C}_{\text{bridg}}\text{–H}$  bond elongation (1.11 Å), relative to the other  $\text{C}_{\text{bridg}}\text{–H}$  bonds (1.09 Å), is observed as a consequence of a slight agostic interaction of the  $\text{CH}_3$  bridging group with the electrophilic Zr center (Structure III). Interestingly enough, the Zr– $\text{C}_{\text{bridg}}$  contact (2.56 Å) is closely comparable to the Zr–O distance found at the  $\mu_3\text{-O2}$  site (2.58 Å; Figure 3), suggesting a comparable ion pair interaction strength. This is a clear indication that in both cases electrostatic interactions are dominant (*vide infra*).

**Ion Pair Interaction Energetics.** In homogeneous olefin polymerization processes, both monomer uptake and insertion are crucial steps for propagation of the polymer chain. Both steps are likely to be influenced by the mobility and coordinative strength of the counteranion, since a strongly bound and immobile anion cannot provide space and suitable acceptor orbitals for incoming olefin activation.<sup>18,19</sup> Likewise, the interaction of the previously described zirconocenium adsorbate species with the surface coordination sites could modulate the kinetics of single-site olefin polymerization processes as well as the product polyolefin microstructure. In the present comparisons, interaction strengths with the surface are analyzed in terms of both formation enthalpies ( $\Delta H_{\text{form}}$ ; eq 1) and heterolytic ion pair separation enthalpies ( $\Delta H_{\text{ips}}$ ; eq 2) for the chemisorbed species. The ion pair formation energy represents an index of the ion pair stability relative to noninteracting reagents as expressed by eq 1. The ion pair separation energy provides a precise indication of the binding strength, and hence of the mobility, of the ions in the adduct (eq 2). Particular attention will be devoted to analysis of the ion pair separation energetics computed for slight displacement of the ions within the adduct,



**Table 3.** Calculated Ion Pair Formation Enthalpies,  $\Delta H_{\text{form}}$  (kcal/mol), and Heterolytic Ion Pair Separation Enthalpies,  $\Delta H_{\text{ips}}$  (kcal/mol), for Activation of  $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$  on the  $\text{Al}_2\text{O}_3$  (110) Surface

	Zr–O distance <sup>a</sup> (Å)	$\Delta H_{\text{form}}$	$\Delta H_{\text{ips}}$
$\mu_3$ -O dioxo-bridged	2.82	–16.7	77.2
$\mu_3$ -O oxo-bridged	2.58	–21.7	82.1
$\mu_2$ -O dioxo-bridged	2.34	–51.7	112.2
$\mu_2$ -O oxo-bridged	2.13	–73.3	127.5
homogeneous adduct	2.56 <sup>b</sup>	–1.7	77.0

<sup>a</sup> In the case of dioxo-bridged structures, a mean distance is considered. <sup>b</sup> The value refers to the Zr–C<sub>bridge</sub> distance shown in Structure III.

since this process is closely correlated with important aspects of the kinetic behavior of the present catalytic systems.

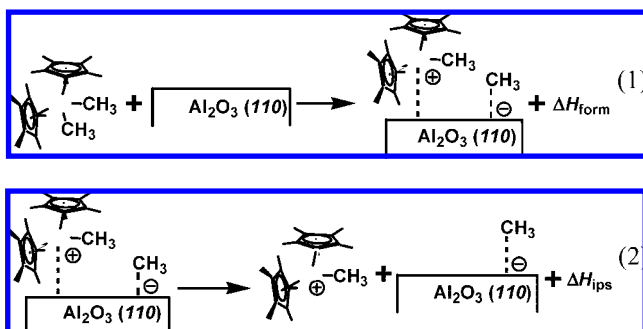
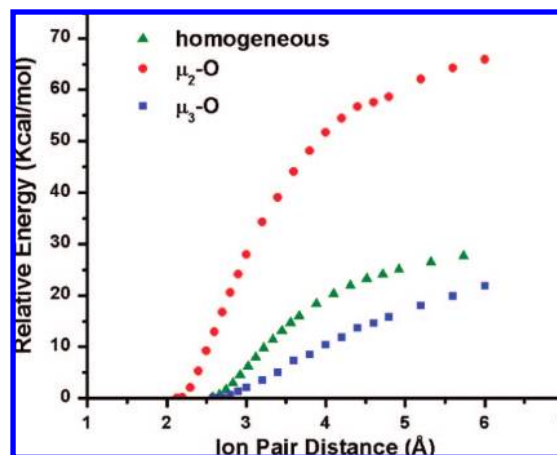


Table 3 compares trends in Zr–O distances in the chemisorbed configurations for both formation and heterolytic ion pair enthalpies. Table 3 clearly shows that there is a correlation between the strength of the interaction and the Zr–O distance. Moreover, there is a general correlation between  $\Delta H_{\text{form}}$  and  $\Delta H_{\text{ips}}$  values even though ion pair dissociation does not represent the microscopic reverse of the ion pair formation process. Thus, the energy gained upon ion pair formation inversely parallels the energetic cost associated with separation into the ionic components. In particular, interactions associated with the  $\mu_2$ -O sites are significantly greater than those found with the  $\mu_3$ -O sites (Table 3) due to the stronger coordinative capability of the  $\mu_2$ -O site versus the  $\mu_3$ -O site. Moreover, interactions found in oxo-bridged configurations are significantly stronger than those in the dioxo-bridged, both in the  $\mu_3$ -O and  $\mu_2$ -O cases (Table 3).

Table 3 shows that, on passing to the homogeneous  $\text{Cp}_2\text{ZrCH}_3^+\text{H}_3\text{CB}(\text{C}_6\text{F}_5)_3^-$  system, the adduct formation process is less exothermic ( $\Delta H_{\text{form}} = -1.7$  kcal/mol) than in the heterogeneous cases. The more acidic character of the alumina surface  $\text{Al}_{\text{III}}$  species versus the homogeneous  $\text{B}(\text{C}_6\text{F}_5)_3$  cocatalyst better stabilizes the methide abstraction product in the heterogeneous case versus the homogeneous analogue. The ion pair mobility of the homogeneous adduct, as indexed by  $\Delta H_{\text{ips}}$ , is comparable to that in the heterogeneous  $\mu_3$ -O dioxo-bridged case (Table 3). Since the total separation of the anion from the cation is a process unlikely to occur during the olefin insertion event that, in turn, involves only slight reorganization of the ion pair (Coulombic interactions dominate during olefin insertion),<sup>19b,h</sup> the energetic changes upon slight displacement of the adsorbate species from the alumina surface are analyzed for the oxo-bridged configurations at both  $\mu_2$ -O and  $\mu_3$ -O donor sites and compared with that of the related homogeneous system. Obviously, the energy values reported in Figure 5 are significantly



**Figure 5.** Energetic demands in the heterolytic ion pair separation process for surface-anchored zirconocenium adsorbate species (eq 2) and for  $\text{Cp}_2\text{ZrCH}_3^+\text{H}_3\text{CB}(\text{C}_6\text{F}_5)_3^-$  in homogeneous solution. The ion pair distances are the Zr–O distance for the heterogeneous cases and the Zr–C<sub>bridge</sub> distance for the homogeneous case.

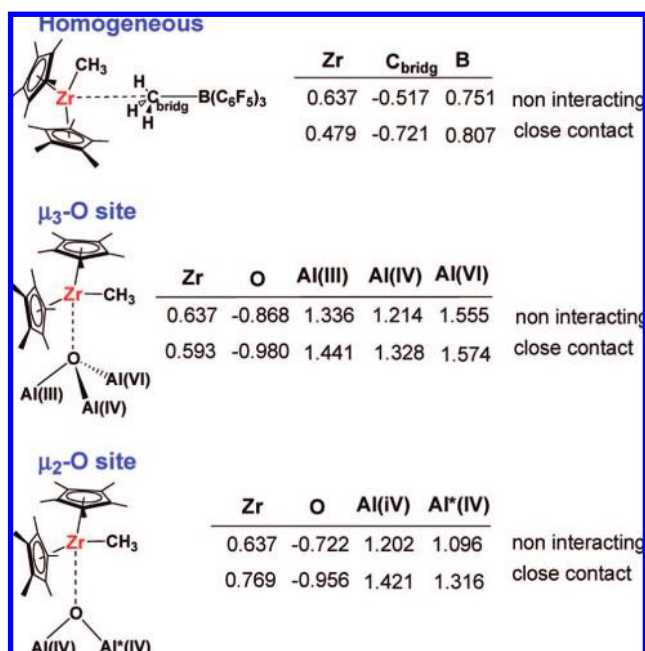
lower with respect to the values associated with the complete ion separation process reported in Table 3 due to the slight displacement of the adsorbate species from the alumina surface with respect to the ideal infinite distance associated with the complete ion separation. The energetic demands associated with further separation of the heterogeneous “ion pair”, however, lead to the  $\Delta H_{\text{ips}}$  values reported in Table 3. In all cases, the energetic profiles present an initial, nearly linear trend paralleling the Zr–O/Zr–C<sub>bridge</sub> contact breaking. After that, a Coulomb-like parabolic trend, mediated by electrostatic interactions, is observed (Figure 5). The heterogeneous catalytic results agree well with the existing theoretical analysis of the parent homogeneous systems.<sup>19b,j,31</sup> In particular, Figure 5 reveals a rapid energy increase in the initial linear portion of the plot as a consequence of the covalent contribution to the Zr–O ion pair interaction at the  $\mu_2$ -O site. Moreover, the Zr–O distance calculated for the oxo-bridged configuration at the  $\mu_2$ -O site (2.13 Å) is compatible with strong donation to the electrophilic Zr center that involves some orbital overlap contribution. For the ion pair interaction at the  $\mu_3$ -O site and for the homogeneous case, a similar initial trend is less evident (Figure 5), suggesting a minor covalent contribution. It is worthy of note that, for the heterogeneous  $\mu_3$ -O case, smaller energetic demands than those in the homogeneous ion pair is observed (Figure 5), even though the contact distances are comparable (Table 3).

This intriguing behavior finds a close counterpart in the atomic charge distributions computed for the homogeneous and heterogeneous cases. In the homogeneous and  $\mu_3$ -O cases, the interaction between the zirconocenium species and the basic counteranion places increased the negative charge density on the donor atoms (C<sub>bridge</sub> in the homogeneous system, the O center in the heterogeneous case) and, conversely, greater positive charge density on the acceptor center of the counteranion (the B atom in the homogeneous case, Al atoms in the heterogeneous case). Furthermore, ion pair contact decreases the positive charge on the Zr center in both cases (Scheme 1). In fact, charge polarization directed toward the cationic center occurs as a consequence of the electrophilic/unsaturated zirconocenium character. Focusing on the Zr center charge, this modification

(31) (a) Vanka, K.; Xu, Z.; Seth, M.; Ziegler, T. *Top. Catal.* **2005**, *34*, 143–164.



**Scheme 1.** Charge Distributions Associated with the Closer Contact and Noninteracting Configurations in Oxo-Bridged Adsorbate Species at both Alumina  $\mu_3$ -O and  $\mu_2$ -O Sites and for the Parent Homogeneous  $\text{Cp}_2\text{ZrCH}_3^+\text{H}_3\text{CB}(\text{C}_6\text{F}_5)_3^-$  Ion Pair



of the charge distribution induced by the ion pair contact becomes more pronounced in the homogeneous case than in the  $\mu_3$ -O heterogeneous case (Scheme 1). The stronger donation in the  $\mu^3$  methyl-bridged homogeneous ion pair versus the Zr-oxide interaction associated with the heterogeneous  $\mu_3$ -O case is largely responsible for the observed energetic trends.

In the  $\mu_2$ -O case, a different charge distribution is observed on passing from the noninteracting to the contact ion pair configuration (Scheme 1). The ion pair contact induces an increased positive charge on the Zr center and an increased negative charge on the coordinated oxide ion. This trend is a consequence of the covalent nature of the Zr-O interaction (*vide supra*). In this case, in fact, the bonding electron pair is shifted toward the oxygen atom due to the electronegativity difference between Zr and O. The greater covalent contribution for the Zr-O interaction in the  $\mu_2$ -O case versus the analogous  $\mu_3$ -O and the homogeneous cases evident in the energetic considerations (*vide supra*) is paralleled by the charge distributions (Scheme 1). It will be seen that these results are key to understanding the observed catalytic properties of these catalysts.

**Ethylene Polymerization Process.** The classic Cossee-Arlman olefin enchainment pathway<sup>32</sup> is considered here (Scheme 2). The Cossee mechanism involves a two-step sequence: (i) olefin coordination to a vacant catalytic site and (ii) alkyl migration of the  $\sigma$ -coordinated polymeryl chain to the  $\pi$ -coordinated olefin. In the present contribution, the most important structural factors and the energy profiles for the ethylene insertion process are analyzed for the dioxo- and oxo-bridged configurations at both  $\mu_3$ -O and  $\mu_2$ -O coordination sites of the  $\gamma$ -alumina surface and compared to the parent homogeneous  $\text{Cp}_2\text{ZrCH}_3^+\text{H}_3\text{CB}(\text{C}_6\text{F}_5)_3^-$  system.

The various steps of the olefin activation and enchainment process are analyzed in the following discussion.

**Adsorbate  $\pi$ -Complexes.** At all coordination sites (dioxo and oxo configuration on both  $\mu_3$ -O and  $\mu_2$ -O) on the  $\gamma$ -alumina surface, the Zr-O distances increase versus those in the starting adsorbate complex, thus allowing the olefin coordination (Table 4). This Zr-O bond elongation is similar in all cases and ranges from 2.5 to 2.8 Å. Negligible distortions of the bond lengths and bond angles within the  $\text{Cp}_2\text{ZrCH}_3^+$  framework are observed upon ethylene binding. The coordinated olefin lies parallel to the Zr-Me vector (the Zr-C1-C2-C3 torsional angle ranges from  $-6.6^\circ$  to  $27.9^\circ$ ). In the dioxo and oxo configuration at the  $\mu_3$ -O site and in the dioxo configuration at the  $\mu_2$ -O site, all the Al-O distances involved in the Zr-ethylene coordination contract, thus restoring the values to those in the noninteracting sites. This is, of course, a consequence of the strong interactions of the cationic metal center with the electron-donating olefin. Clearly, electronic saturation of the Zr center due to olefin coordination is the key factor driving the surface geometrical rearrangement.

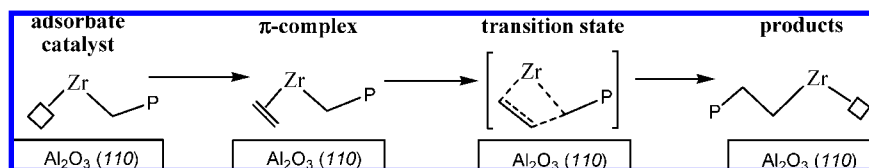
In contrast to the above results, the oxo-bridged configuration at the  $\mu_2$ -O site does not follow this trend on ethylene binding because of the very large surface distortion arising from the interaction with the zirconocenium adsorbate. Thus, the Al-O distances remain comparable to those found in the starting adsorbate species. Finally, in the  $\mu_2$ -O dioxo-bridged configuration, the surface interaction between the Cp ring and the Al<sub>III</sub> center (*vide supra*) is lost because the zirconocenium center is displaced from the surface (see the Zr-O3 and Zr-O4 distances in Table 4) upon ethylene coordination.

On passing to the homogeneous case,  $\pi$ -complex formation involves a reorientation of the methylborate counteranion. In particular, the  $\mu$ -CH<sub>3</sub> bridging is lost to minimize nonbonded interactions (Table 5). Nevertheless, the olefin lies parallel to the Zr-Me vector as observed for the heterogeneous cases. Negligible differences in  $\text{Cp}_2\text{ZrCH}_3^+$  ligation metrics are detected between the homogeneous and heterogeneous cases in terms of bond distances and angles.

**Insertion Transition States.** In all of the present cases, homogeneous and heterogeneous, both a Zr-methyl C3-H bond elongation (1.13–1.14 Å) relative to the other C-H bonds (1.09 Å) and distortion (from tetrahedral) of the  $\angle\text{Zr-C3-H1}$  bond angle to  $68.6^\circ$ – $75.5^\circ$  are observed as a consequence of an  $\alpha$ -agostic assisted olefin insertion pathway. The geometrical parameters indicate a stronger agostic interaction for insertions at  $\mu_2$ -O sites than at  $\mu_3$ -O sites (Table 6). Analysis of the transition state geometries reveals a coplanar arrangement of the four Zr-C1-C2-C3 centers (Table 6) and concerted bond forming/breaking sequences at both coordination sites. In fact, the Zr-C1, C1-C2, C2-C3, Zr-C3 bond lengths all exhibit intermediate values between those in the starting  $\pi$ -complexes and in the kinetic insertion products (*vide infra*), indicating synchronous scission of the Zr-C3 bond (2.32–2.36 Å) and elongation of the C=C double bond (C1-C2 = 1.41–1.42 Å) to form a C-C single bond and a new Zr-C1  $\sigma$ -bond (Zr-C = 2.45–2.41 Å).

Focusing first on the heterogeneous cases, the alumina surface metrical parameters exhibit negligible geometrical variations relative to the initial  $\pi$ -complexes. The Zr-O distances slightly increase for the dioxo configurations ( $\Delta_{\text{mean}} = 0.38$  Å for the  $\mu_3$ -O site and 0.49 Å for the  $\mu_2$ -O site) and for the oxo configuration on the  $\mu_3$ -O site ( $\Delta = 0.23$  Å) versus the initial  $\pi$ -complexes because of the greater steric crowding around the zirconocenium center in the transition states. The oxo-bridged configuration at the  $\mu_2$ -O site does not follow this trend ( $\Delta =$

(32) (a) Cossee, P. *J. Catal.* **1964**, *3*, 80–88. (b) Arlman, E. J.; Cossee, P. *J. Catal.* **1964**, *3*, 99–104.

**Scheme 2.** Cossee–Arlman Mechanism for Heterogeneous Olefin Polymerization**Table 4.** Geometrical Parameters for the Chemisorbed Zirconocenium Olefin  $\pi$ -Complex Structures (Å or deg)

Zr adsorbate at the alumina $\mu_3$ -O site		
	dioxo-bridged	oxo-bridged
Zr-Cp <sub>centr</sub>	2.26	2.25
Zr-C1	2.80	2.84
Zr-C3	2.31	2.30
C1-C2	1.36	1.36
C2-C3	3.19	3.24
$\angle$ Cp-Zr-Cp	133.9°	132.2°
$\angle$ Zr-C1-C2-C3	3.2°	9.2°
Zr-O1	5.50	7.26
Zr-O2	5.41	5.30
Zr adsorbate at the alumina $\mu_2$ -O site		
	dioxo-bridged	oxo-bridged
Zr-Cp <sub>centr</sub>	2.25	2.25
Zr-C1	2.84	2.85
Zr-C3	2.30	2.29
C1-C2	1.37	1.36
C2-C3	3.31	3.39
$\angle$ Cp-Zr-Cp	135.2°	132.2°
$\angle$ Zr-C1-C2-C3	-6.6°	27.9°
Zr-O3	5.22	6.27
Zr-O4	5.04	4.60

0.02 Å) because of the large surface distortion described above. In the case of the homogeneous ion pair, the Zr–B distance in the transition state structure increases relative to the  $\pi$ -complex (Table 5) due to the greater steric crowding around the Zr center, similar to the Zr–O distance trend in the aforementioned heterogeneous cases.

**Insertion Products.** The kinetic insertion products (Figure 6) exhibit, in all homogeneous and heterogeneous cases, C3–H1 bond elongation (1.13 Å) relative to the other C–H bonds (1.10 Å) and a distortion of the  $\angle$ Zr–C1–C2 bond angle from tetrahedral due to an  $\gamma$ -agostic interaction (Table 7). The distortion of the  $\angle$ Zr–C1–C2 bond angle is more evident for

**Table 5.** Geometrical Parameters for the  $\pi$ -Complex, Insertion Transition State, and Product Structures for the Ethylene Insertion at the Homogeneous  $\text{Cp}_2\text{ZrCH}_3^+\text{H}_3\text{CB}(\text{C}_6\text{F}_5)_3^-$  Ion Pair (in Å or deg)

$\pi$ -complex		insertion TS	
Zr-Cp <sub>centr</sub>	2.25		2.27
Zr-C1	2.91		2.37
Zr-C3	2.29		1.44
C1-C2	1.36		1.43
C2-C3	3.29		2.24
$\angle\text{Cp-Zr-Cp}$	132.6		129.7
C3-H1	1.11		1.14
$\angle\text{Zr-C3-H1}$	112.6		73.8
$\angle\text{Zr-C1-C2-C3}$	1.2		-17.3
Zr-B	7.40		7.48
$\gamma$ -product		$\beta$ -products	
Zr-Cp <sub>centr</sub>	2.22		2.22
Zr-C1	2.28		2.29
Zr-C3	2.85		3.89
C1-C2	1.56		1.53
C2-C3	1.56		1.54
$\angle\text{Cp-Zr-Cp}$	133.3		135.4
C3-H1	1.12		1.10
C2-H2	1.10		1.16
$\angle\text{Zr-C1-C2}$	94.9		85.6
Zr-B	6.85		6.85

the insertions at  $\mu_2$ -O sites than at  $\mu_3$ -O sites as was observed in the transition states discussed above, indicating a stronger agostic interaction at the  $\mu_2$ -O sites than at the  $\mu_3$ -O sites. In the homogeneous case, the distortion of the Zr-C1-C2 bond angle is comparable to that observed at the  $\mu_3$ -O sites (Table 5). In the case of the dioxo-bridged configuration at  $\mu_2$ -O sites, a further interaction is observed between the complex and the surface (Figure 6). This interaction involves the C3-H bond and the O4 ion and is supported by elongation of the C3-H3 bond (1.13 Å) with respect to the other C3-H bonds (1.10 Å). The rotation of the *n*-propyl group (growing polymer chain) about the C1-C2 axis creates another bonding configuration for all heterogeneous cases (Figure 6, Table 7). In these new conformations, there is evidence of C2-H2 bond elongation (to 1.16–1.17 Å) compared to the other C-H bonds (1.10 Å) and of a  $\angle\text{Zr-C1-C2}$  bond angle distortion from tetrahedral

(Table 7), due to formation of  $\beta$ -agostic interactions. Similar modifications are also observed in the homogeneous case (Table 5).

Finally, in the case of the dioxo-configuration at the  $\mu_2$ -O site, a pronounced approach of the Zr catalyst toward the surface is observed versus the  $\pi$ -complex structure. This observation is supported by the contracted Zr-O distances ( $\Delta_{\text{mean}} = -0.58$  Å). Negligible variations in the Zr-O distances are observed in the other cases.

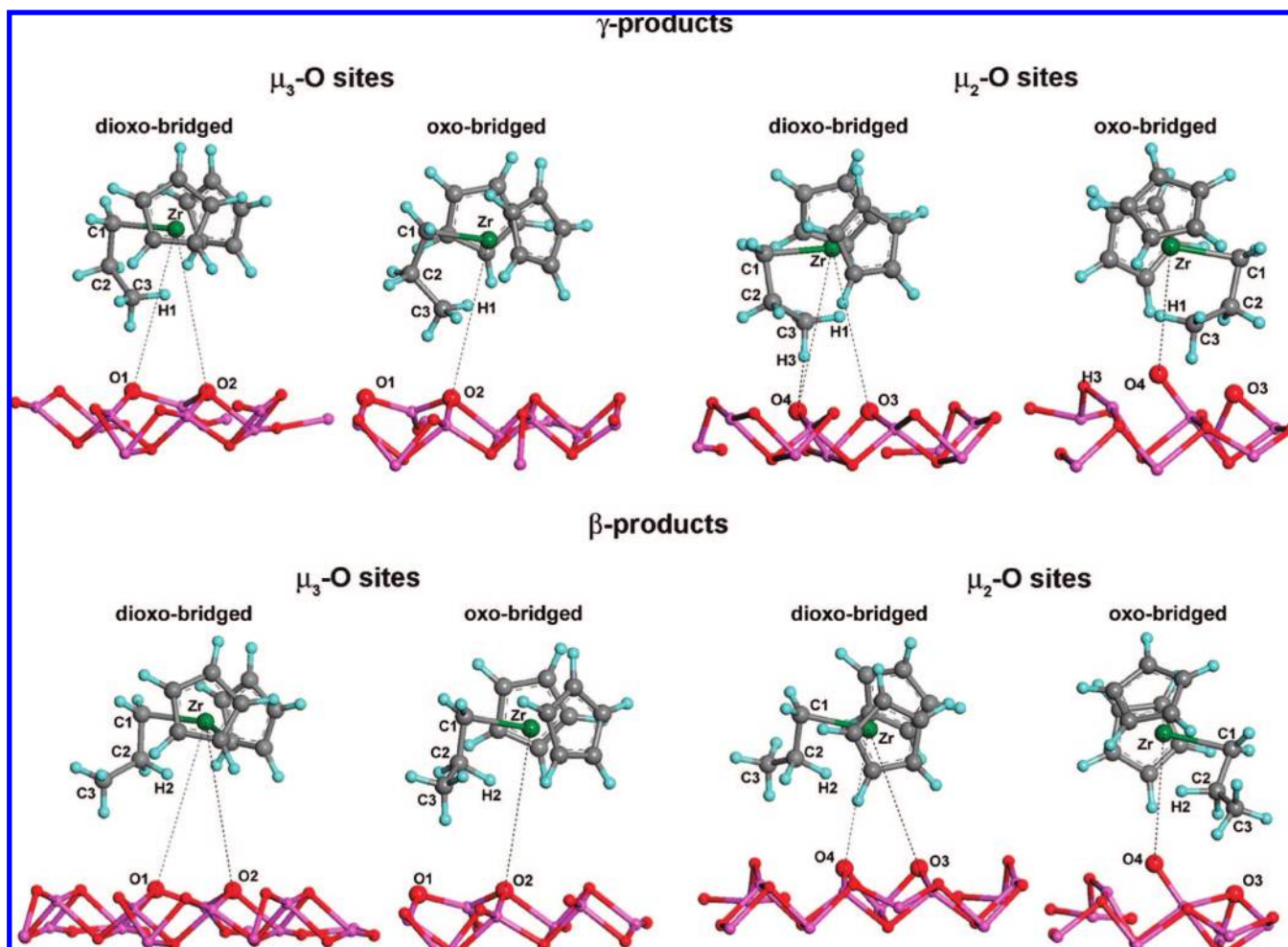
**Energetics of the Ethylene Insertion Processes.** Energetic analysis of the ethylene activation/insertion profiles (Figure 7) affords the following observations. Ethylene  $\pi$ -complex formation incurs a large enthalpic penalty at the  $\mu_2$ -O coordination site ( $\Delta E = +40.3$  and  $+42.7$  kcal/mol for the dioxo- and oxo-bridged configurations, respectively). In marked contrast, only  $+5.5$  and  $+8.5$  kcal/mol are required for ethylene activation at the  $\mu_3$ -O coordination site for dioxo- and oxo-bridged configura-

**Table 6.** Geometrical Parameters of the Insertion Transition State Structures (in Å and deg)

Zr adsorbate on $\mu_3$ -O site		
	dioxo-bridged	oxo-bridged
Zr-C <sub>pcentr</sub>	2.25	2.25
Zr-C1	2.45	2.41
Zr-C3	2.33	2.36
C1-C2	1.41	1.42
C2-C3	2.30	2.20
$\angle$ Cp-Zr-Cp	133.5	134.2
C3-H1	1.13	1.13
$\angle$ Zr-C3-H1	75.5	70.1
$\angle$ Zr-C1-C2-C3	-5.4	-6.7
Zr-O1	5.83	6.66
Zr-O2	5.84	5.53
Zr adsorbate on $\mu_2$ -O site		
	dioxo-bridged	oxo-bridged
Zr-C <sub>pcentr</sub>	2.25	2.25
Zr-C1	2.41	2.42
Zr-C3	2.32	2.32
C1-C2	1.42	1.42
C2-C3	2.20	2.22
$\angle$ Cp-Zr-Cp	134.3	134.4
C3-H1	1.14	1.14
$\angle$ Zr-C3-H1	68.6	68.9
$\angle$ Zr-C1-C2-C3	-13.9	6.2
Zr-O3	5.65	6.24
Zr-O4	5.58	4.58

tions, respectively (Figure 7). Interestingly, the insertion profiles associated with the oxo configurations are at substantially higher energies than those associated with the corresponding dioxo configurations at both the  $\mu_3$ -O and  $\mu_2$ -O coordination sites. This trend is due to the stronger Zr-complex/surface interaction in the oxo configuration than in the dioxo configuration. Note that once the energies of the  $\pi$ -complexes are taken as zero reference levels, the overall energetics of the ensuing steps (transition state and products) are closely comparable. In particular, the energy barriers associated with the  $\mu_2$ -O sites are slightly lower than those associated with the  $\mu_3$ -O sites (6.0–6.2 vs 8.1–8.4 kcal/mol). These differences can be associated with stronger agostic interactions in the  $\mu_2$ -O transition state structures than in those

at the  $\mu_3$ -O sites (*vide supra*). The  $\gamma$ -agostic product associated with the insertion pathways at the  $\mu_3$ -O sites exhibits a similar stabilization energy for dioxo- and oxo-bridged configurations (–5.8 and –5.4 kcal/mol, respectively). In the case of  $\mu_2$ -O sites, –12.5 and –8.3 kcal/mol stabilization energies are associated with the dioxo- and oxo-bridged configurations, respectively. The greater stabilization observed for the dioxo-bridged product is clearly due to the additional interaction between the C3–H bond of the Zr catalyst center and the O4 ion of the surface (*vide supra*). The  $\beta$ -agostic products exhibit comparable stabilization energies, ranging from –12.1 to –13.7 kcal/mol. In the dioxo-bridged configuration at the  $\mu_2$ -O site, a greater stabilization energy is observed (–18.8 kcal/mol) as a



**Figure 6.** Ethylene insertion product structures for the zirconocenium dioxo- and oxo-bridged configurations at  $\mu_3$ -O and  $\mu_2$ -O sites.

**Table 7.** Computed Geometrical Parameters for the Ethylene Insertion Product Structures (in Å and deg)<sup>a</sup>

	zirconocenium adsorbate on $\mu_3$ -O site				zirconocenium adsorbate on $\mu_2$ -O site			
	dioxo-bridged		oxo-bridged		dioxo-bridged		oxo-bridged	
	$\gamma$ -product	$\beta$ -product	$\gamma$ -product	$\beta$ -product	$\gamma$ -product	$\beta$ -product	$\gamma$ -product	$\beta$ -product
Zr–C <sub>pcentr</sub>	2.24	2.23	2.24	2.22	2.25	2.23	2.24	2.23
Zr–C1	2.29	2.29	2.28	2.30	2.24	2.29	2.25	2.29
Zr–C3	2.82	3.93	2.75	3.88	2.56	3.91	2.64	3.89
C1–C2	1.56	1.53	1.56	1.52	1.57	1.53	1.57	1.52
C2–C3	1.56	1.54	1.56	1.54	1.57	1.54	1.57	1.54
$\angle$ Cp–Zr–Cp	134.4	136.8	134.3	137.3	132.6	134.4	134.5	136.2
C3–H1	1.13	1.10	1.13	1.10	1.13	1.10	1.13	1.10
C2–H2	1.10	1.17	1.10	1.17	1.10	1.16	1.10	1.16
$\angle$ Zr–C1–C2	95.5	85.8	93.9	85.7	85.9	85.3	88.3	84.8
Zr–O <sub>x</sub> <sup>b</sup>	5.68	5.72	6.70	6.60	5.44	4.75	6.24	6.19
Zr–O <sub>y</sub> <sup>b</sup>	5.92	5.89	5.44	5.36	5.37	4.36	4.47	4.43

<sup>a</sup> Labeling refers to Figure 6. <sup>b</sup> *x* and *y* are, respectively, 1 and 2 for the  $\mu_3$ -O site and 3 and 4 for the  $\mu_2$ -O site.

consequence of the previously described, closer approach of the catalyst to the alumina surface.

In the present heterogeneous catalytic olefin enchainment scenario, note that  $\pi$ -complex formation represents the discriminating step in overall catalytic activity for ethylene polymerization among the different zirconocene chemisorption sites. Furthermore, closer analysis of the  $\pi$ -complex formation step for the oxo-bridged configurations at both  $\mu_3$ -O and  $\mu_2$ -O coordination sites reveals a correlation between the computed

ion-pair separation energies ( $\Delta H_{\text{ips}}$ ) and the  $\pi$ -complex formation energies. In particular, there is an approximately linear correlation between the two parameters (Figure 8). Note that the energetics of the dioxo-bridged configuration at the  $\mu_2$ -O site do not adhere to this linear trend (Figure 8). This energetic deviation can be attributed to the additional interaction between the zirconocenium Cp ligand and the surface Al<sub>III</sub> Lewis acid site discussed above (Figure 4). In this case, displacement of the zirconocenium catalyst due to olefin coordination requires

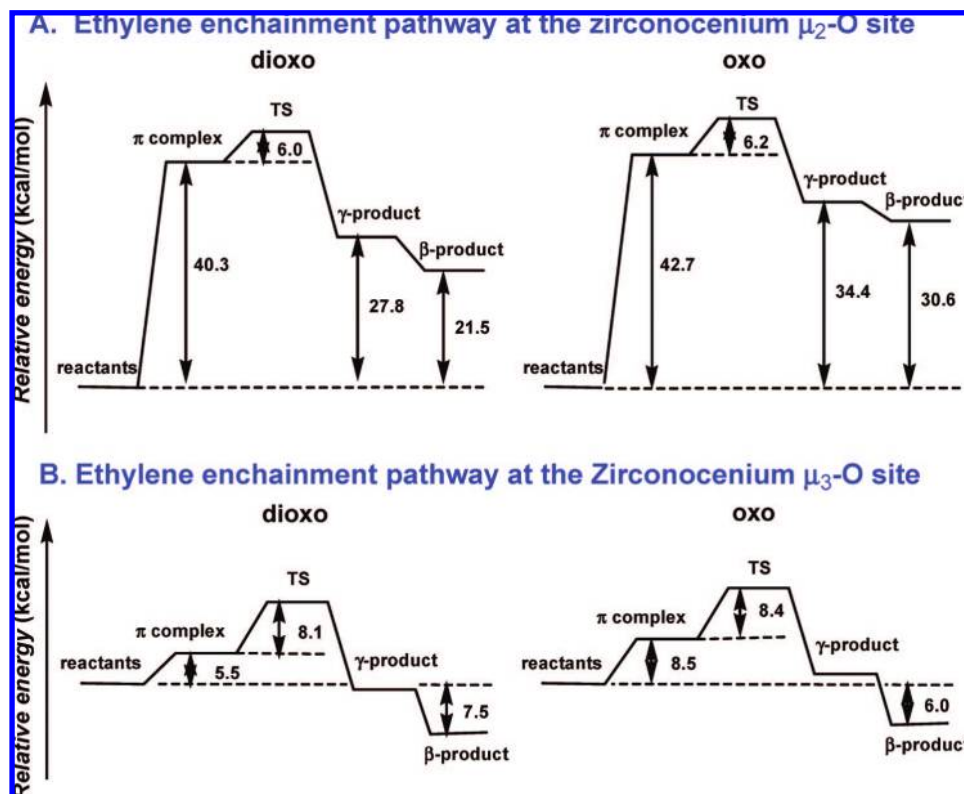


Figure 7. Ethylene insertion energetic profiles at  $\text{Cp}_2\text{ZrCH}_3^+$  species bound to the (A)  $\mu_2\text{-O}$  and (B)  $\mu_3\text{-O}$  sites of the  $\gamma$ -alumina (100) surface.

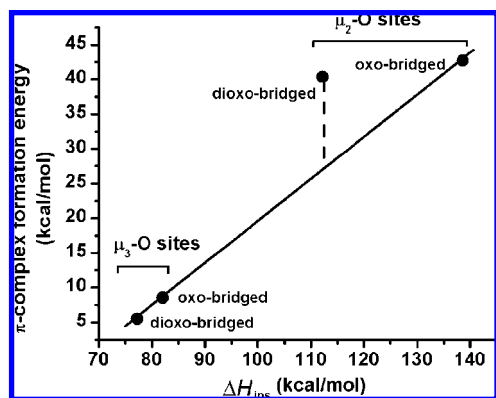


Figure 8. Ethylene  $\pi$ -complex formation energy at the various  $\text{Cp}_2\text{ZrCH}_3^+$  surface coordination sites as a function of the ion pair separation enthalpy.

additional disruption of this Lewis acid–base interaction, hence an additional 15 kcal/mol.

#### Heterogeneous vs Homogeneous Polymerization Processes.

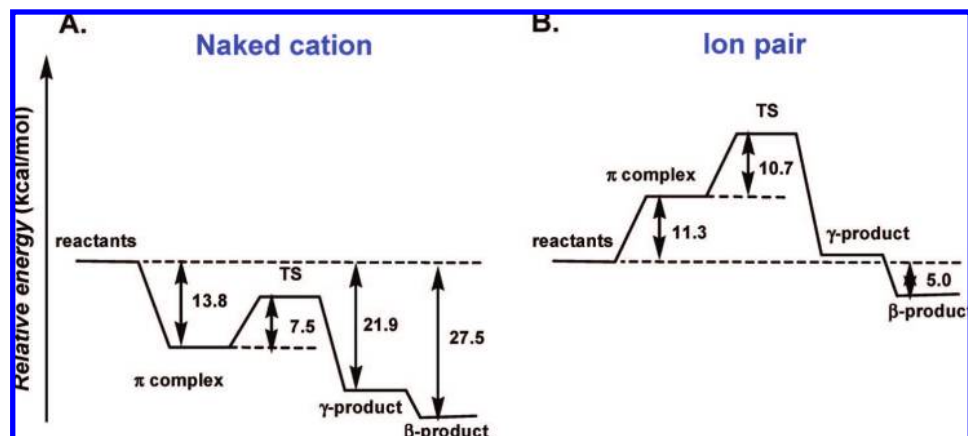
The surface ethylene insertion process analyzed for the present heterogeneous system can now be compared/contrasted with the analogous process involving the homogeneous phase  $\text{Cp}_2\text{ZrCH}_3^+\text{H}_3\text{CB}(\text{C}_6\text{F}_5)_3^-$  catalytic system and its related naked cation. In the homogeneous case, the olefin coordination, insertion transition state, and product structures exhibit geometrical trends around the metal center which are surprisingly similar to those in the heterogeneous cases (*vide supra*). In particular, elongation of the ion pair distance is observed in concert with the ethylene  $\pi$ -coordination. Moreover, there is evidence for a four-center transition state assisted by an  $\alpha$ -agostic interaction, resulting in both  $\gamma$ -agostic and  $\beta$ -agostic products.

The insertion energetic profile for the  $\text{Cp}_2\text{ZrCH}_3^+$  naked cation reveals that, in the absence of a counteranion,  $\pi$ -ethylene complex formation results in overall stabilization (Figure 9a), suggesting that the energetic demands observed for  $\pi$ -complex formation in all the other cases are associated with displacement of the counteranion (the surface for the heterogeneous system, the borate in the homogeneous system; Figures 7, 9b). The insertion energy describing the homogeneous ion pair enchainment pathway (Figure 9b) shows that the energy required for  $\pi$ -complex formation (11.3 kcal/mol) lies between the values found in the two heterogeneous cases (40.3 and 42.7 kcal/mol for  $\mu_2\text{-O}$  sites, and 5.5 and 8.5 kcal/mol for  $\mu_3\text{-O}$  sites). In both the naked and ion paired systems, only minor energetic differences are observed for the subsequent steps (transition state and products) as found in the heterogeneous cases. This observation highlights the energetic importance of the  $\pi$ -complex formation step to the catalytic kinetics.

An important finding of this investigation is that the overall reactivity of the homogeneous zirconocenium system is calculated to be greater than that computed for the heterogeneous  $\mu_2\text{-O}$  site but smaller than that of the heterogeneous  $\mu_3\text{-O}$  site. These trends offer an appealing explanation for two key experimental observations: (1) Only a fraction of the surface sites in such dehydroxylated  $\gamma$ -alumina-supported single-site metallocene catalysts are catalytically significant as deduced by poisoning and solid state NMR dosing experiments.<sup>13–17</sup> (2) Those surface sites which are catalytically significant exhibit significantly greater catalytic activities than their homogeneous analogues.<sup>13–17</sup>

#### Conclusions

The structural and catalytic properties of the organozirconium precatalyst  $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ , chemisorbed on dehydroxylated  $\gamma$ -alu-



**Figure 9.** Ethylene insertion pathways for the homogeneous naked cation (A) and the ion paired (B) zirconocenium catalyst systems.

mina, have been investigated using DFT methods. Specifically, the interaction of the  $\text{Cp}_2\text{ZrCH}_3^+$  adsorbate species with two prototypical surface oxide environments,  $\mu_3\text{-O}$  and  $\mu_2\text{-O}$ , are analyzed, and the geometric and energetic details of ethylene activation and enchainment pathways on these sites have been investigated and compared with the analogous homogeneous processes. It is found that the distinctive catalytic features of the heterogeneous systems are governed largely by the interaction strength between the  $\text{Cp}_2\text{ZrCH}_3^+$  adsorbate species and the various, structurally distinct surface oxide sites. The detailed analysis of the ion pair interactions for the most representative coordinating  $\text{Al}_2\text{O}_3$  surface oxide sites is compared to ion pair interactions in the related homogeneous zirconocenium system. It is concluded that the fundamental role played by the nature and strength of such interactions dominates the rate of catalytic olefin polymerization. Experimental evidence for the structures of the catalytically active surface sites and of the greater activity of certain heterogeneous sites vs their homogeneous analogues is well-supported by the present theoretical results. Moreover, our theoretical approach explains key factors, mechanistic and energetic, associated with the unusual catalytic behavior of these single-site heterogeneous systems. The complete delineation of

heterogeneous catalytic structure–reactivity relationships presents an enormous challenge due to difficulties associated with their unambiguous experimental characterization. In this context, the present results represent to our knowledge the first theoretical/computational attempt to analyze metallocene single-site phenomenology associated with olefin polymerization processes on oxide surfaces and, hence, should provide a starting point for a complete understanding of such systems and how they differ from their homogeneous analogues.

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**Supporting Information Available:** Possible geometry configurations of the homogeneous  $\text{Cp}_2\text{ZrCH}_3^+\text{H}_3\text{CB}(\text{C}_6\text{F}_5)_3^-$  ion pair adduct (Figure S1). A complete list of Cartesian coordinates of all structures presently analyzed. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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