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Highly Electrophilic Olefin Polymerization Catalysts. Counteranion and Solvent Effects on Constrained Geometry Catalyst Ion Pair Structure and Reactivity

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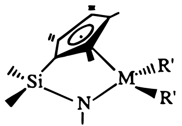
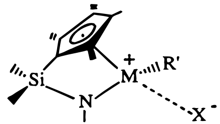
Single-site group 4 "constrained geometry catalysts" (CGCs, e.g. **I**) currently attract attention as highly efficient and selective agents for producing polyolefins having unprecedented/useful architectures and processing characteristics.[1,2] The active species are thought to consist of cation−anion pairs (e.g. **II**), and growing experimental evidence indicates that the nature of such ion pairing, as modulated by cocatalyst/counteranion (X^-)[3] and solvent,[4] has significant consequences for catalyst activity, chain transfer characteristics, and possibly stereoselectivity. In contrast to experimental efforts, theoretical studies of such catalysts, while greatly expanding our understanding, have focused almost exclusively on naked group 4 cations.[5−7] We communicate here preliminary results of the first ab initio computational investigation, including counteranion and solvation, of catalyst generation, catalyst−cocatalyst structural energetics, and the olefin activation/insertion reaction coordinate for a CGC-based ion pair; it is seen that counteranion and solvation effects are substantial.

I



II



Calculations were performed at the MP2/HF level on a model CGC structure (geometries optimized at the HF level using gradient techniques; energies refined at the MP2 level).[8] Solvent effects were modeled using the self-consistent isodensity polarized continuum formalism.[9] First, catalyst-generating eq 1 was

$$H_2Si(C_5H_4)(^tBuN)Ti(CH_3)_2 + B(C_6F_5)_3 \rightarrow \underset{\mathbf{1}}{H_2Si(C_5H_4)(^tBuN)Ti(CH_3)^+CH_3B(C_6F_5)_3^-} \quad (1)$$

investigated in vacuo. The calculated enthalpy, −10 kcal/mol, is in reasonable agreement with experiment (−22.6(7) kcal/mol for the Me_4C_5 analogue),[10] and inclusion of solvent (C_6H_6; $\epsilon = 2.274$) improves the agreement (−13 kcal/mol). Gradient geometry optimization of **1** yields a μ-Ti···H_3C−B geometry (Figure 1; C(2) methyl hydrogens bent toward Ti) with computed metrical parameters in favorable agreement with diffraction results for $(CH_3)_2Si[(CH_3)_4C_5](^tBuN)\ Ti(CH_3)^+CH_3B(C_6F_5)_3$[11] (**2**; Ti−C(1) = 2.087(4), Ti−C(2) = 2.364(3), C(2)−B = 1.675(5) Å). The present calculations and orbital population analysis indicate that the Ti−methyl interaction is best described as η^3-H_3C−B.

Heterolytic separation of the **1** ion pair in vacuo (eq 2) is calculated to be very endothermic (+78 kcal/mol) in agreement

$$H_2Si(C_5H_4)(^tBuN)Ti(CH_3)^+CH_3B(C_6F_5)_3^- \rightarrow H_2Si(C_5H_4)(^tBuN)Ti(CH_3)^+ + CH_3B(C_6F_5)_3^- \quad (2)$$

with recent DFT results for heterolysis of $Cp_2M(CH_3)^+(CH_3)_2AlCl_2^-$ (∼+100 kcal/mol).[7] Inclusion[9] of solvation (C_6H_6) in eq 2 reduces the endothermicity to +43 kcal/mol, still substantially in excess of experimental $\Delta H^\ddagger$ values for ion-pair-separating symmetrization detectable by dynamic NMR in aromatic solvents (∼+15 kcal/mol for **2**;[10] +15−20 kcal/mol for typical metallocenes[3b,10]). Analysis of the solvation effects reveals (Table 1), not surprisingly, that charged species are stabilized most.[12] Since $(CH_3)_2Si[(CH_3)_4C_5](^tBuN)Zr(CH_3)^+B(C_6F_5)_4^-$ forms an isolable

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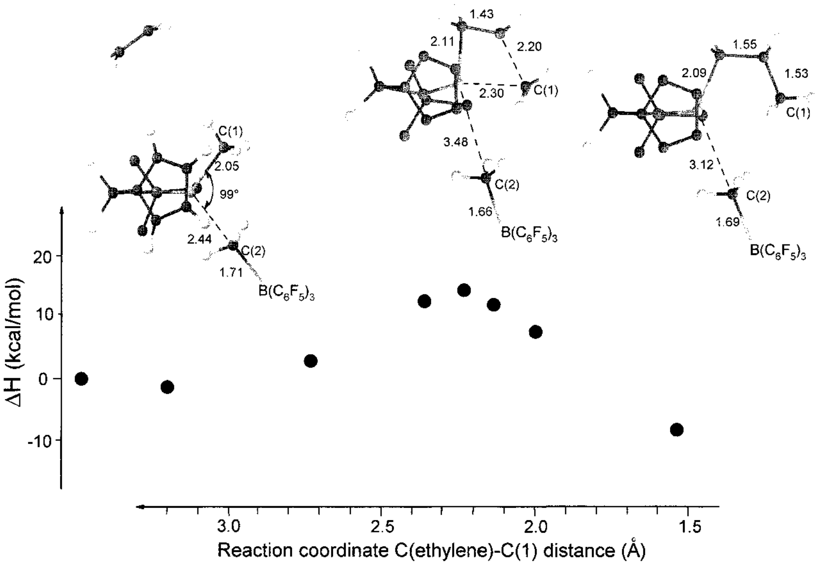


Figure 1. Computed energies of olefin activation and insertion for the reaction $H_2Si(C_5H_4)({}^tBuN)Ti(CH_3)^+(CH_3)B(C_6F_5)_3^-$ (**1**) + ethylene. The reference point for the energy scale is for the isolated reagents, and nonspecific benzene solvation is included.

Table 1. Computed[a] Stabilization Energies (kcal/mol) on Passing from the Gas Phase to Benzene Solution

$H_2Si(C_5H_4)({}^tBuN)Ti(CH_3)^+CH_3B(C_6F_5)_3^-$	10
$H_2Si(C_5H_4)({}^tBuN)Ti(CH_3)^+$	28
$CH_3B(C_6F_5)_3^-$	17
$H_2Si(C_5H_4)({}^tBuN)Ti(CH_3)_2$	1
$B(C_6F_5)_3$	6

[a] Using the approach of ref 9.

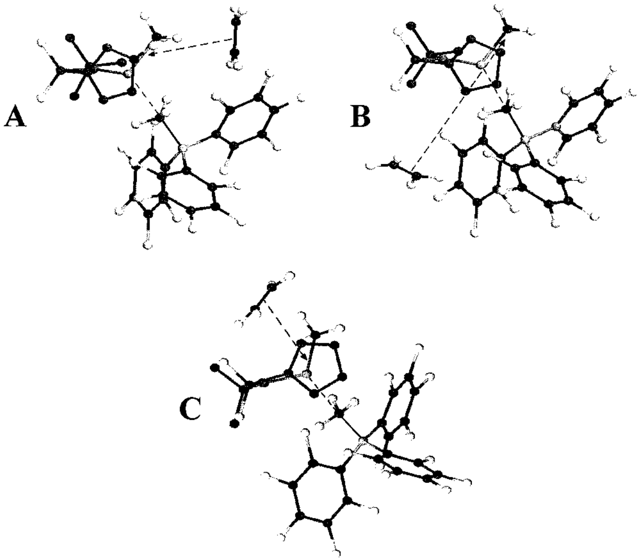
η^n-toluene complex,[3b] calculations were next carried out including Ti−η^n-C_6H_6 complexation (n = 3 was of lowest energy; eq 3).

$$H_2Si(C_5H_4)({}^tBuN)TiCH_3{}^+CH_3B(C_6F_5)_3{}^- \xrightarrow{C_6H_6} H_2Si(C_5H_4)({}^tBuN)Ti(CH_3)^+{\cdot}C_6H_6 + CH_3B(C_6F_5)_3{}^- \quad (3)$$

In this case, the computed ion pair dissociation enthalpy is reduced to +23 kcal/mol. These results argue that, especially in saturated hydrocarbon solvents,[1,2] chain propagation is unlikely to involve completely separated ion pairs and that solvation effects are non-negligible.

In regard to **1**-mediated ethylene activation and insertion, three pathways were initially considered (Scheme 1). Of these, Hartree−Fock-level calculations rule out **A** and **B** as energetically unreasonable. Concerted pathway **C** involving olefin activation and insertion distal to the $CH_3B(C_6F_5)_3^-$ group was next investigated in detail (Figure 1). The vector denoting progressive formation of the new C−C bond ($Ti(CH_3)-H_2C{=}CH_2$) was taken as the reaction coordinate, and the energy profile evaluated by varying the C(1)−C(ethylene) distance while optimizing all other geometrical parameters and imposing no constraints. The MP2 energetic trends (including nonspecific solvation) reveal a rather flat profile in early stages of reaction with a relatively low energy transition state at C−C = 2.20 Å (+14 kcal/mol—in reasonable agreement with the limited available data[13]). As ethylene approaches, a synchronous bending of the Ti−CH_3 vectors with respect to the Ti−N−Si plane is observed (Ti−C(1) toward; Ti−C(2) away). At the transition state, Ti−C(1) lies essentially in the Ti−N−Si plane, ∠C(1)−Ti−C(2) has contracted to 72°, and Ti···C(2) has elongated to 3.48 Å. At the transition state, ethylene is part of a puckered (~10°) four-membered ring with C−C contacts to Ti and C(1) of 2.11 and 2.20 Å, respectively. Metrical parameters in the inserted n-propyl kinetic product are generally similar to **1** except for a 0.64 Å lengthening of Ti···C(2), presumably to accommodate the bulky n-propyl group and possible weak γ-agostic interactions. No intermediates are detected along the reaction coordinate.

Scheme 1



These results provide the first quantitative theoretical information on bonding, structural energetics, and olefin chemistry of CGC ion pairs. For all of these characteristics, the roles of counteranion and solvent are energetically important and cannot be ignored. The further consequences of these factors for olefin polymerization processes are under continuing investigation.

Acknowledgment. We thank MURST (I.L.F.), CNR (I.L.F.), and DOE (T.J.M., Grant 86ER13511) for support of this research.

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(12) Solvation effects (experimental) for coordinatively saturated metallocenium ions are ~20−40 kcal/mol (polar solvents) and ~15−30 kcal/mol (nonpolar solvents): Richardson, D. E.; Alameddin, N. G.; Ryan, M. F.; Hayes, T.; Eyler, J. R.; Siedle, A. R. *J. Am. Chem. Soc.* **1996**, *118*, 11244 and references therein.

(13) (a) Sernetz, F. G.; Mülhaupt, R.; Waymouth, R. M. *Macromol. Chem. Phys.* **1996**, *197*, 1071. $E_a \approx 14$ kcal/mol for $(CH_3)_2Si[(CH_3)_4C_5]({}^tBuN)TiCl_2$/MAO-mediated ethylene + styrene copolymerization. (b) Chien, J. C. W.; Razavi, A. *J. Polym. Sci. A*, **1988**, *26*, 2369. $E_a \approx 7$ kcal/mol for $(neomenthylC_5H_4)_2ZrCl_2$/MAO-mediated ethylene polymerization. (c) Ishihara, A.; Jia, L.; Marks, T. J., manuscript in preparation. $E_a \approx 2-10$ kcal/mol for $L_2Zr(CH_3)_2/B(C_6F_5)_3$-mediated ethylene polymerization (L = various cyclopentadienyl ligands).