Communications

Why Is β-Me Elimination Only Observed in d^0 Early Transition Metal Complexes? An Organometallic Hyperconjugation Effect with Consequences for the Termination Step in Ziegler–Natta Catalysis

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Summary: Two processes, β-H and β-Me migration, have been observed to compete in the termination of alkene oligomerization (Ziegler–Natta catalysts) in certain d^0 early transition metal systems. ECP ab initio calculations have been performed to study these processes. Models of intermediates (X_2MR^q: $X = Cl, Cp; M = Zr, Hf, Ti, q = +1; Zr, Nb, q = 0$) have been optimized at the HF level with additional single-point energy calculations at the MP2 level. It is shown that the β-Me elimination may be thermodynamically favored over β-H elimination for strongly electron-deficient metal centers. This preference is attributed to the presence of multiple bonding between a d^0 transition metal and the methyl group, which behaves like a weak π donor via its occupied π_{CH_3} orbitals. It is therefore analogous to the well documented hyperconjugation in organic chemistry.

Electron-deficient transition metal alkyl complexes usually undergo β-H elimination. Recently, however, an increasing number of cases of β-Me migration have been reported.[1] These have been exclusively limited to cyclo-pentadienyl derivatives of d^0 early transition metals: Zr(IV), Hf(IV), Ln(III) (Ln = La, Nd, Lu), and Sc(III). All these systems are usually thought of as promoting olefin oligomerization. Since it is well accepted that the activation of the C–C bond is more difficult than that of C–H,[2] this process has attracted considerable interest and has been interpreted in terms of steric constraints.[1] Since only d^0 complexes appear to be able to activate a C–C bond, electronic factors may also play a role. Understanding the factors which control this β-H/β-Me competition may thus become important in chain-length determination in Ziegler–Natta catalytic systems.

Previous theoretical studies have investigated olefin insertion into M–H or M–Me bonds and the tacticity of

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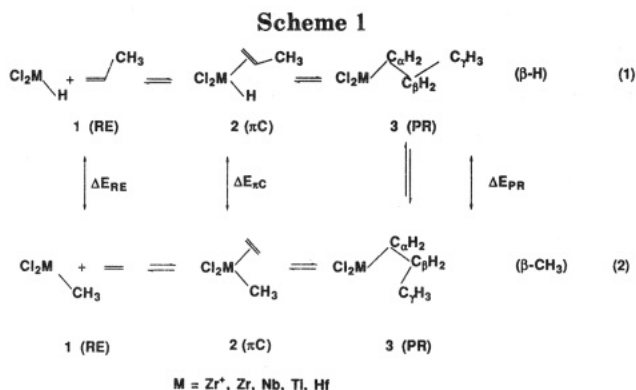(4) (a) Jolly, C. A.; Marynick, D. S. J. Am. Chem. Soc. 1989, 111, 7968. (b) Castonguay, L. A.; Rappé, A. K. J. Am. Chem. Soc. 1992, 114, 5832. (c) Kawamura-Kuribayashi, H.; Koga, N.; Morokuma, K. J. Am. Chem. Soc. 1992, 114, 2359, 8687. (d) Prosenc, M.-H.; Janiak, C.; Brintzinger, H.-H. Organometallics 1992, 11, 4036. (e) Mohr, R.; Berke, H.; Erker, G. Helv. Chim. Acta 1993, 76, 1389. (f) Ziegler, T.; Folga, E.; Berces, A. J. Am. Chem. Soc. 1993, 115, 636. (g) Siegbahn, P. E. M. Chem. Phys. Lett. 1993, 205, 290; J. Am. Chem. Soc. 1993, 115, 5803. (h) All these studies are based on the Cossee mechanism: Cossee, P. J. Catal. 1964, 3, 80.

Scheme 1

$$Cl_2M \cdot \underset{H}{+} \ \overset{CH_3}{=} \ \rightleftharpoons \ Cl_2M \underset{H}{\overset{CH_3}{\diagup}} \ \rightleftharpoons \ Cl_2M \overset{C_\alpha H_2}{\diagdown} \underset{C_\beta H_2}{\overset{C_\gamma H_3}{}} \quad (\beta\text{-}H) \quad (1)$$

1 (RE)   2 (πC)   3 (PR)

ΔE_{RE} $\Delta E_{\pi C}$ ΔE_{PR}

$$Cl_2M \cdot \underset{CH_3}{+} \ = \ \rightleftharpoons \ Cl_2M \underset{CH_3}{\overset{}{\diagup}} \ \rightleftharpoons \ Cl_2M \overset{C_\alpha H_2}{\diagdown} \underset{C_\beta H_2}{\overset{C_\gamma H_3}{}} \quad (\beta\text{-}CH_3) \quad (2)$$

1 (RE)   2 (πC)   3 (PR)

M = Zr$^+$, Zr, Nb, Tl, Hf

Figure 1. Difference in energies (ΔE_{RE}, $\Delta E_{\pi C}$, ΔE_{PR}) in kcal/mol for the three intermediates **1**, **2**, and **3** shown in Scheme 1.

the growing polymers.[3,4] However, the competitive (β-H/β-Me migration) reactions which terminate the chain-growing process have not yet been understood and are addressed in this paper.

The intermediates **1**, **2**, and **3**, corresponding respectively to the 14-electron reactant (RE), the 16-electron complex (π-C), and the 14-electron polymerization product (PR) postulated by the Cossee mechanism,[4h] are given in eqs 1 and 2 of Scheme 1 (β-H and β-Me elimination, respectively). These systems have been calculated by core potential (ECP) *ab initio* calculations using the GAMESS set of programs.[5] Pseudopotentials were chosen for Zr, Nb,[6a] and Cl.[6b] The metal valence shells were described by a (5s/3,1,1), (5p/3,1,1), (4d/3,1) basis set[6a] and a (4s/3,1), (4p/3,1) basis set for Cl.[6b] Cp* was modeled by Cl. Double-ζ basis sets were used for C and H[6c] with added polarization functions ($\zeta = 0.75$ and $\zeta = 1.0$, respectively). Additional calculations using Cp in place of Cl have also been performed on some selected structures. All species have been optimized with the gradient method at the HF level, with subsequent single-point energy calculations performed at the MP2 level. The nature of the minima was assigned by Hessian calculations. The relative energies of the two RE species were not significantly affected when calculated at the MP4 level. The results of the calculations in terms of ΔE_{RE}, $\Delta E_{\pi C}$, and ΔE_{PR} at the MP2 level are shown in Figure 1.

Results and Discussion. We concentrate here on the Cl_2ZrR^+ (R = H, Me) systems. The geometries of all the structures are in close agreement with those of previously calculated related structures. In particular, the Zr center is pyramidal in structures **1** and **3**. Full details can be found in the supplementary material.

The conformation of the propyl chain in the products (PR) has no great influence on the total energy of these species. The most stable conformation corresponds to an eclipsed chain which brings the C_β–C_γ bond into an agostic situation (C_β–C_γ = 1.607 Å, Zr–C_α–C_β = 91°, C_α–C_β–C_γ = 124°). Other conformations with the staggered alkyl chain, or with an agostic C_β–H in the equatorial plane, are calculated to be about 4 kcal/mol higher. Although these small energy differences may be modified by the substitution of Cl by other groups, no large energy differences
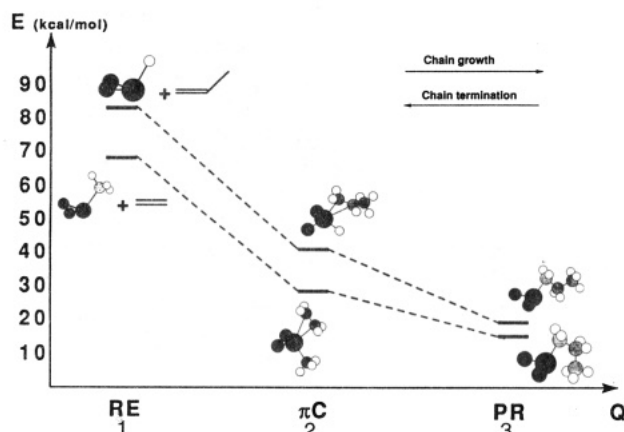
between these conformations are expected. The structures best suited for β-Me and β-H migrations are thus of similar energies.

Upon β-migration, the two olefin products (π-C) differ more in energy; that produced by β-Me migration is lower than that resulting from β-H migration ($\Delta E_{\pi C} = 12.3$ kcal/mol). Loss of olefin reveals an even greater preference for the Me species in the resultant metal fragments ($\Delta E_{RE} = 18.0$ kcal/mol).[7]

In our model system, the formation of Zr–Me$^+$ and C–H bonds is thermodynamically preferred to that of Zr–H$^+$ and C–Me bonds, suggesting that, other factors being equal, β-Me elimination will be favored over β-H elimination. Since the C–H bond in ethene is approximately 10 kcal/mol stronger than C–Me in propene, the Zr–Me$^+$ bond is stronger than Zr$^+$–H by about 2 kcal/mol in π-C and 8 kcal/mol in RE. Previous *ab initio* calculations on cationic and neutral M–H and M–Me bond energies[8] show the Zr–Me$^+$ bond to be 0.6 kcal/mol stronger than Zr–H$^+$ in the case of the naked metal. Therefore, the change of ligand field which influences the s, p, d mixing and the oxidation of the metal upon ligation by Cl increases the difference between the two bond energies.

Why should the Zr–Me$^+$ bond be stronger than the Zr–H$^+$ bond in our systems? One possible reason could be the presence of an empty d shell which, in an electron-deficient transition metal complex, can interact with the lone pair(s) of a π-donor ligand (halide, OR, NR$_2$, ...) to form metal–ligand multiple bond(s). Such interactions increase significantly the stability of unsaturated complexes.[9] We suggest that the occupied π_{CH_3} orbitals may act as weak π-donating orbitals. This is an extension of the hyperconjugation effect which is widely invoked in organic chemistry to explain the stability of carbocations.

The empty d orbitals of a d^0 X$_2$M fragment are well suited for establishing multiple bonding with a π-donor

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(7) One also notes that the chain-growth (π-C into PR) process is slightly exothermic and that the bond dissociation energy of the olefin from RE is modest (around 30 kcal/mol). These two facts come from the lack of back-donation into the olefin. If the π-C complexes were much more stable than RE because of back-donation (the case for a non-d^0 system), the polymerization might be disfavored. No Ziegler–Natta catalysis takes place with Nb(III).

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ligand. The π bond between the LUMO of the d^0 X_2M metal fragment and π_{CH_3} in the mirror plane of X_2M-Me (C_s symmetry) is shown in 4. The other π_{CH_3} orbital can only overlap with a much higher empty orbital of the metal fragment.

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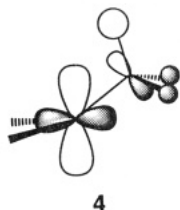
Since CH_3 is a weak π donor, many other factors can influence the difference in energy between the M–H and M–Me bonds. However, if such donation is important, increasing the electron density at the metal should tend to increase the preference for H, since the weak electron donation from CH_3 may be replaced by electron repulsion between the electrons of the metal and those of π_{CH_3}. Our calculations support this idea, since all ΔE values decrease with respect to the reference ΔE_{RE} value obtained in the case of the Cl_2ZrR^+ metal fragment when electron density is augmented at the metal center. Thus, adding a ligand to the metal by the coordination of an olefin to Cl_2ZrR^+ ($\Delta E_{\pi C}$ = 12.3 kcal/mol), increasing the electron donation ability of the coordinated ligands by substituting Cp for Cl (ΔE_{RE} = 8.0 kcal/mol), or adding one or more electrons as in neutral Cl_2ZrR (ΔE_{RE} = 8.6 kcal/mol) or Cl_2NbR (ΔE_{RE} = 5.8 kcal/mol) will each diminish or even reverse the difference in energy between M–Me and M–H bonds calculated in the case of Cl_2ZrR^+. In contrast, Cl_2HfR^+ behaves like Zr(IV) (ΔE_{RE} = 19.2 kcal/mol and $\Delta E_{\pi C}$ =

10.9 kcal/mol) as it retains the same electronic and structural environment.[10] All our results are consistent with the experimental observation that decreasing the electron density of the metal augments the M–Me bond energy.[11]

In conclusion, we suggest that this stabilizing metal–Me hyperconjugation, which requires both a d^0 metal and empty metal orbitals of proper symmetry to receive electrons from the π_{CH_3} orbital(s), will play a role in favor of β-Me migration. This hyperconjugation is not limited to the calculated structures but will be active throughout the reaction path. However, as in organic chemistry, it is a small effect which may be offset by other factors (steric constraints and relative activation energies for the metal insertion into C_β–H and C_β–Me bonds). Thus, these other factors may be important in the case of Ti(IV), since according to our calculation Cl_2Ti^+ could also induce a preference for β-Me migration (ΔE_{RE} = 26 kcal/mol and $\Delta E_{\pi C}$ = 14 kcal/mol).[10] We propose, however, that the metal–Me hyperconjugation effect should play a role, albeit sometimes latent, in highly oxidized early transition metal chemistry. Other examples in addition to those described here may become apparent in the future.

Supplementary Material Available: Drawings of and a list of Cartesian coordinates for the RHF-optimized structures (8 pages). Ordering information is given on any current masthead page.

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