1. (5 pts) In metallocene-catalyzed ethylene polymerization, when Hf and Zr complexes with the same ligand are compared,
   (a) Molecular weight of the polyethylene formed is greater for Hf than for Zr
   (b) Catalyst activity (rate of PE formation) is greater for Zr than for Hf
   Explain these observations.

2. (10 pts) McConville reported the first example of living polymerization of an aliphatic α-olefin at room temperature:

   ![Chemical Structure]

   Ar = 2,6-(i-Pr)₂C₆H₃ or Ar = 2,6-(Me)₂C₆H₃
   R = n-Pr, n-Bu, n-Hex

   (a, 1 pt) Plot the expected relationship between molecular weight and time for an idealized living polymerization. What is the expected distribution of molecular weight values for the polymer product?
   (b, 1 pt) Suggest a structure for the active catalyst.
   (c, 2 pts) Predict the effect on polymerization catalysis if the bulky N-aryl groups were replaced by unsubstituted Ph groups. Explain your answer in terms of a mechanism for the polymerization, with comparison to the Brookhart/DuPont late metal polymerization catalysts.
   (d, 2 pts) When MAO was used as a co-catalyst instead of the borane, molecular weight was reduced, polydispersity increased, and NMR analysis of the polymer showed no olefinic end groups. Explain these observations in terms of a mechanism for the polymerization, with special attention to the termination step.
   (e, 2 pts) When CH₂Cl₂ is added to reaction mixtures, the catalyst activity and hence polymer molecular weight increases. Activity increases by a factor of about 10, and molecular weight by a factor of about 30. Give possible explanations for these observations.
   (f, 2 pts) When catalysis is carried out in the presence of toluene, activity decreases. Give a possible explanation for this observation.
3. (10 pts) Schrock recently investigated the dianionic MesNpy ligand (precursor shown below) for olefin polymerization catalysts. Two trigonal bipyramidal precatalysts, [MesNpy]ZrR₂ (R = Me or i-Bu), activated with [Ph₃C][B(C₆F₅)₄], were studied.

![MesNpy ligand structure](image)

(a) For R = Me, the dinuclear cation [[MesNpy]₂Zr₂(Me)₃][B(C₆F₅)₄] (1) is formed; this compound is relatively unreactive to further tritylborate activator (2). A mixture of 1 and 2 polymerizes 1-hexene to high molecular weight, with low polydispersity, but about half of 1 remains unreacted after 160 equiv of 1-hexene has been polymerized. A byproduct in this polymerization is a mixture of cis and trans-2-heptene.

(b) For R = i-Bu, [[MesNpy]Zr(i-Bu)][B(C₆F₅)₄] (3) is formed. This also polymerizes 1-hexene to high MW with low polydispersity, but all of 3 is consumed and there are no low molecular weight byproducts.

**Explain the differences between the Zr-Me and Zr-i-Bu systems in terms of mechanisms for the polymerization and formation of the byproducts.**