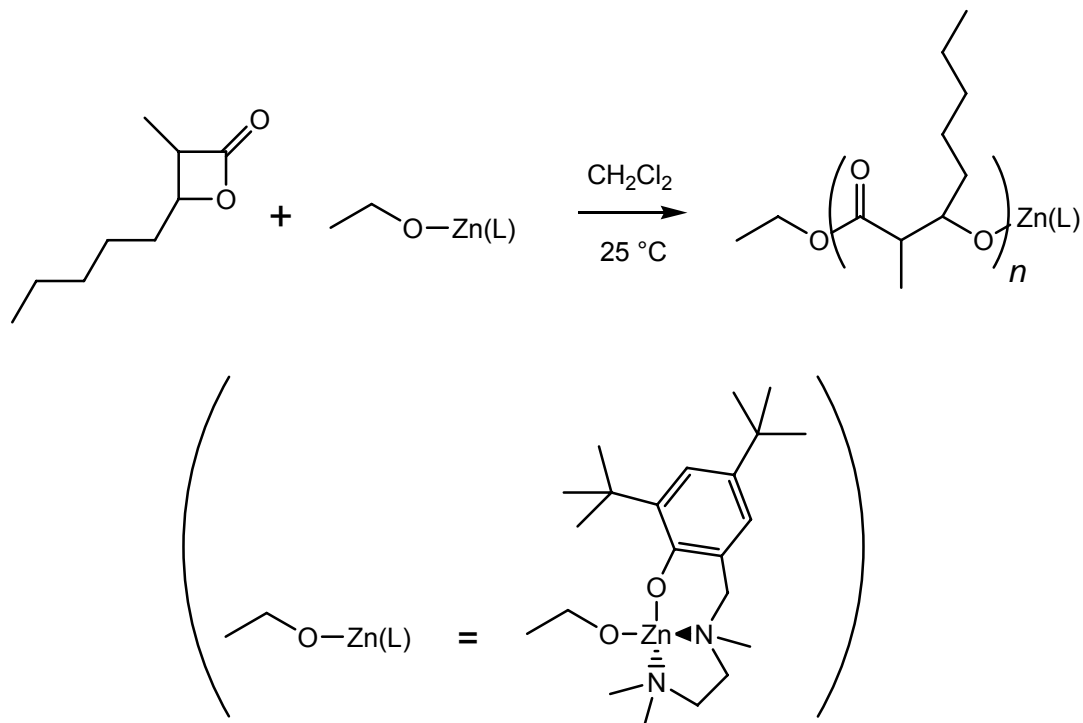


Problem Set 1

Due: In class, Monday, September 19

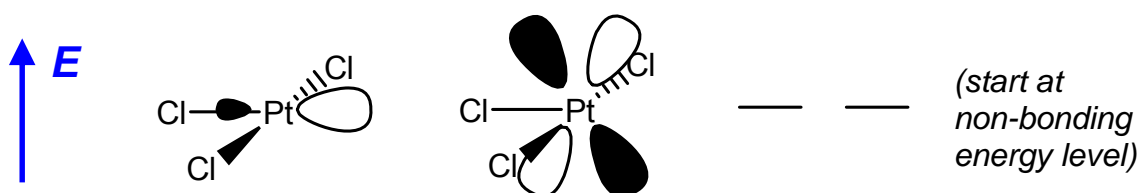
1. Kathleen Schreck (Hillmyer Group) has shown that α -Methyl- β -pentyl- β -propiolactone (MPP) undergoes ring-opening polymerization in the presence of a Lewis-acidic, zinc alkoxide catalyst:¹



- Draw a mechanism, using arrow-pushing, for the $(\text{L})\text{ZnOEt}$ -catalyzed initiation ($n = 1$) of MPP. In this mechanism, you can treat “ Zn(L) ” like you would an acidic proton, and EtOZn(L) like you would EtOH .
- Draw a potential energy diagram for your mechanism, with all of your drawn intermediates represented. Try to make the relative vertical scale of your diagram reasonable—estimate the relative energies for each of the intermediates. How will the energy of the product relate to that of the starting material?
- How do you think the mechanism and potential energy surface for this initiation step compares to the next (propagation, $n = 2$) step?

¹ Schreck, K. M.; Hillmyer, M. A. *Tetrahedron* **2004**, 60, 7177-7185.

2. The bond between Pt and ethylene (C_2H_4) in the complex $PtCl_3(C_2H_4)$ can be described in terms of component molecular orbitals of the $PtCl_3$ and C_2H_4 fragments. The $PtCl_3$ fragment accepts two electrons from the highest occupied molecular orbital (HOMO) of ethylene to fill its 18-electron ($s^2p^6d^{10}$) configuration, and also contributes non-bonding electrons to the lowest unoccupied molecular orbital (LUMO) of ethylene in a stabilizing, “back-bonding” interaction. The participating Pt p and d orbitals look something like:



(The Pt center is square-planar—meaning the three Cl ligands and the Pt lie in the same plane—in this cartoon. Keep in mind, I haven’t drawn the two electrons that the Pt center has to put in the orbitals.)

- Draw π and π^* molecular orbitals for C_2H_4 .
- Now, dock C_2H_4 with the right side of the $PtCl_3$ fragment above in such a way that π -Pt orbital interactions are maximized. Keeping orbital symmetry in mind, which C_2H_4 orbitals will mix with which $PtCl_3$ orbitals?
- Draw an orbital energy diagram that illustrates the orbital mixing in this system. Where do the four electrons (two from the C_2H_4 π orbital, two from the Pt center) end up?

Problems to try on your own:

MPOC, Appendix 5: Problems 1-4.