1. (6 pts) Enantioselectivity in asymmetric catalysis is often ascribed to steric effects. However, electronic effects can also do the job. After consulting this DuPont paper on asymmetric hydrocyanation, [Casalnuovo, A. L.; RajanBabu, T. V.; Ayers, T. A.; Warren, T. H. J. Am. Chem. Soc. 1994, 116, 9869-9882. Ligand Electronic Effects in Asymmetric Catalysis: Enhanced Enantioselectivity in the Asymmetric Hydrocyanation of Vinylarenes. http://dx.doi.org/10.1021/ja00101a007], **explain how the electronic effects of the ligands are proposed to control the ee.**

2. (8 pts) The complex \([\text{Rh(Binap)(OH)}]_2\), which contains bridging hydroxides, is a catalyst precursor for the addition of phenylboronic acid to enones. One example is shown.

The following experimental observations were made:

i. When racemic Binap was used, \(^{31}\text{P}\) NMR spectroscopy showed only one dimer, with the same chemical shift and \(J_{\text{Rh-P}}\) as that for the enantiopure complex; thus, only the RR and SS complexes, and none of the RS, were observed.

ii. This dimer is the resting state during catalysis. The reaction rate shows half-order dependence on the concentration of \([\text{Rh(Binap)(OH)}]_2\).

iii. A **negative** nonlinear effect was observed during catalysis when the ee of Binap in the catalyst precursor was varied.

**Explain** these observations in terms of a mechanism for the reaction.
3. (6 pts) Addition of ZnEt₂ to benzaldehyde is catalyzed by several different amino alcohol ligands (as seen in class for Noyori’s example). A striking ligand effect on the reaction rate was observed: ligands a-c all gave about the same rate, while reaction with ligand d was about 10 times faster. Enantioselectivity was similar for all 4 ligands.

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R = Me (a), CH₂Ph (b), CHPh₂ (c), CPh₃ (d)
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**Explain** these observations in terms of a mechanism for the reaction.

4. (5 pts) Chemists at Merck investigated asymmetric hydrogenation of indole derivative 1, which was found to be in Ru-catalyzed equilibrium with endocyclic isomer 2. As the hydrogen pressure is increased, ee drops; low H₂ pressure was required to maximize ee. Ru(Binap)-catalyzed hydrogenation of 2 was found to be faster than that of 1, and gave high ee without dependence on H₂ pressure, but hydrogenation of 1 was pressure-dependent (higher ee at lower pressure). By considering the relative rates of reaction of 1 and 2 with the Ru catalyst, and the rate of their interconversion, **explain** these observations.