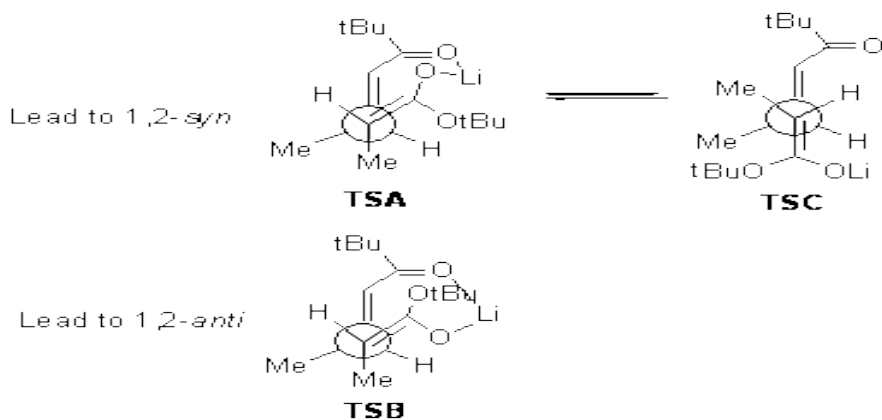
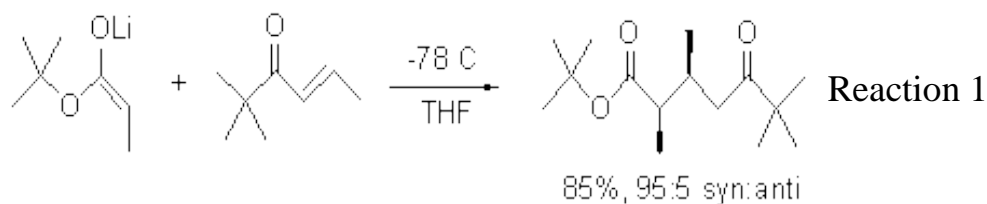
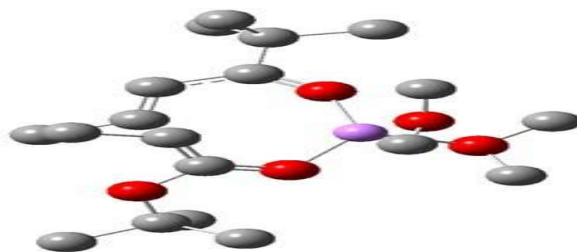


STEREOCHEMISTRY OF THE MICHAEL ADDITION

Heathcock's model for predicting the stereo-outcome of Michael additions¹ involves a metal bridging across the two carbonyl oxygens. For Reaction 1, the model predicts that 1,2-*syn* product over the 1,2-*anti* product based on more favorable steric arrangements in **TSA** relative to **TSB**. Note that other rotatamers of these TS models are possible, but are presumed to be less favorable due to the inability of the metal cation to bridge the carbonyls. In fact, the *syn:trans* ratio for Reaction 1 is 95:5.



Kwan and Evans have examined this (and related) reactions at the M05-2x/6-31G(d) level.² Dimethyl ether is used as the model for the solvent. The lowest energy transition state for Reaction 1 is **TS1**, shown in Figure 1 with suppressed drawing of the hydrogens (though the Jmol active image will include the hydrogens). This structure is actually more like **TSC**, a rotamer that was thought to not have a bridging metal. **TS1** does have the bridging metal, and this is accomplished by having dihedral values of 40° instead of the ideal 60°. So, computations support the general conclusion of the Heathcock approach, with a modification of the possible inclusion of some other rotamers, though the stereoprediction is not altered.



TS1

Figure 1. M05-2x/6-31G(d) optimized structure of the lowest energy transition state of Reaction 1. Hydrogens are removed in the image for clarity, but the Jmol active image (which you can see by clicking on the above image) will include the hydrogen atoms.

Source: <http://comporgchem.com/blog/?p=1233>