

Lanthanocene Complexes as Unique and Selective Catalysts

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Lanthanocene complexes have been shown to catalyze a variety of reactions, including hydrosilylation.¹ Many features of lanthanocenes make them potentially useful catalysts. They are Lewis acids, have high kinetic lability, they are thermally stable over a wide range of temperatures, and they can be readily synthesized.^{2,11} In general, most lanthanides are extremely stable in the Ln^{3+} oxidation state, and the Ln^{3+} ionic radii vary in a systematic way across the series.⁷ The general stability of the Ln^{3+} oxidation state has two consequences: steric properties of a system will have a larger net effect, and oxidative addition and reductive elimination mechanistic routes are inaccessible and other mechanisms must be proposed. Many postulated mechanisms have involved 4-center transition states as shown in Figure 1.^{3,4,5}



Figure 1

The systematic change in ionic radii allows the steric properties of a system to be “tuned” by changing the lanthanide.¹² This can be demonstrated by an examination of hydrosilylation of alkenes and alkynes. Hydrosilylation is the addition of H-Si across a carbon-carbon double or triple bond. This addition can be made in a Markovnikov (2,1 addition) or anti-Markovnikov (1,2 addition) fashion. For small lanthanides and group three metals (e.g. Lu, Y, Yb, or Y) addition of H_3SiPh across a terminal double bond (1-decene) yields 100% anti-Markovnikov addition product. Using larger lanthanides (e.g. La or Nd) generates as much as 44% Markovnikov product.⁶ The steric environment can also be altered by use of an *ansa*-bridged ligand system, as shown in Figure 2.⁹ By comparison the percent anti-Markovnikov product for Cp^*_2LnR versus $(\text{Me}_2\text{Si})\text{Cp}^*_2\text{LnR}$ (as shown in Figure 2), it is evident that when Ln is Sm or Nd the selectivity for anti-Markovnikov addition is greatly reduced (from 92% to 33% and 76% to 33% respectively).⁶ In hydrosilylation of styrene the same trends for metal and ligand effects are observed, but the Markovnikov product is much more strongly favored in less sterically crowded species. This is postulated to be due to a π -interaction between the lanthanide and the phenyl group of the styrene.⁵ Hydrosilylation of alkynes is affected to a smaller degree than for alkenes because alkynes are less sterically demanding substrates.⁴

Selectivity for the least hindered alkene in a diene is observed in the $\text{Cp}^*_2\text{YMe}(\text{THF})$ catalyst system (yields up to 96% are observed).¹⁰ Dienes and enynes reacting in less sterically crowded catalysts systems can undergo cyclization first, and then hydrosilylation.³

This reaction was taken advantage of in the synthesis of (\pm) Epilupinine. The penultimate step of the synthesis is carried out using 5% Cp*₂YMe(THF) as a catalyst giving an overall yield of 84% and greater than 95% of the desired isomer.⁸

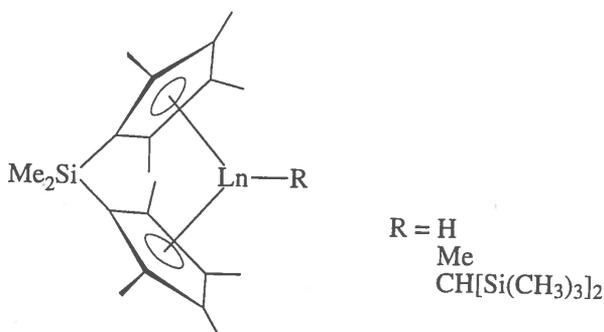


Figure 2

Mechanistic investigation of the hydrosilylation reaction was undertaken to distinguish between mechanisms postulating a Ln-H active catalyst and a Ln-Si active catalyst. This was done by studying the cyclization/hydrosilylation of 1,5-hexadiene. The major product predicted by the Ln-H mechanism ((silylmethyl)cyclopentane) is consistent with the experimentally observed products while the major product predicted by the Ln-Si mechanism (1-methyl-3-silylcyclopentane) is not observed at all.

Careful choice of lanthanide and ligand system allows “tuning” of the steric properties of a lanthanocene catalyst system. This “tunability” of lanthanocene catalyst systems has been demonstrated to have a marked affect on the regiochemistry of hydrosilylation reaction products. This approach should be generally applicable to other lanthanocene-based catalytic reactions.

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