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Demystifying $Cp_2Ti(H)Cl$ and its enigmatic role in the reactions of epoxides with Cp_2TiCl

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The role of $Cp_2Ti(H)Cl$ in the reactions of Cp_2TiCl with trisubstituted epoxides has been investigated in a combined experimental and computational study. Although $Cp_2Ti(H)Cl$ has generally been regarded as a robust species, its decomposition to Cp_2TiCl and molecular hydrogen was found to be exothermic ($\Delta G = -11$ kcal/mol when the effects of THF solvation are considered). In laboratory studies, $Cp_2Ti(H)Cl$ was generated using the reaction of 1,2-epoxy-1-methylcyclohexane with Cp_2TiCl as a model. Rapid evolution of hydrogen gas was measured, indicating that $Cp_2Ti(H)Cl$ is indeed a thermally unstable molecule, which undergoes intermolecular reductive elimination of hydrogen under the reaction conditions. The stoichiometry of the reaction (Cp_2TiCl:epoxide = 1:1) and the quantity of hydrogen produced (1 mol per 2 mol of epoxide) is consistent with this assertion. The diminished yield of allylic alcohol from these reactions under the conditions of protic versus aprotic catalysis can be understood in terms of the predominant titanium(III) present in solution. Under the conditions of protic catalysis, Cp_2TiCl complexes with collidine hydrochloride and the titanium(III) center is less available for “cross-disproportionation” with carbon-centered

radicals; this leads to byproducts from radical capture by hydrogen atom transfer, resulting in a saturated alcohol (2-methylcyclohexan-1-ol).