

UV/Vis Spectroscopic Investigations in Homogeneous Catalysis

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Introduction

Using a fibreoptical optrode gives the possibility to use UV/Vis spectroscopy for the determination of rate and equilibrium constants under anaerobic conditions. We will present some investigations in ligand exchange processes on rhodium complexes. Already in 1977 Halpern et al. described stable η^6 bridged arene complexes.[1] These arene complexes (formed for example in aromatic solvents (see Figure 1)) can decrease the activity of asymmetric hydrogenations.[2] Knowing stability constants for this kind of arene complexes allows the optimization of reactions even when aromatic substrates are used. Therefore we will present a static and a dynamic way to determine stability constants for several rhodium-ligand-arene systems.

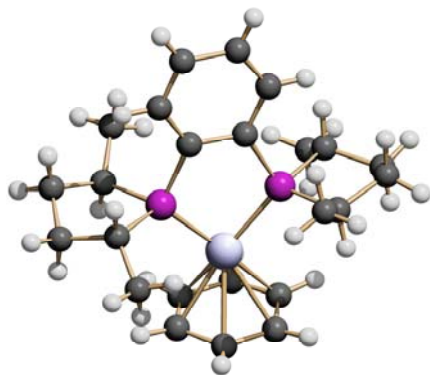


Figure 1. X-Ray Structure of $[\text{Rh}((R,R)\text{-MeDuPHOS})(\text{benzene})]^+$.

Results and Discussion

Application of cationic rhodium catalysts containing a diolefin causes distinctive induction periods in the asymmetric hydrogenation of prochiral olefins.[3] Such induction periods, which lead to a decreased activity, are caused by the fact that parts of the catalyst concentration are blocked for the actually interesting hydrogenation of the prochiral olefin. That is, these parts are inactive due to coordination of the diolefin ligand. Because of the relatively slow COD hydrogenation the share of active catalyst increases at first, typical induction periods result.

From a practical standpoint the question needs to be addressed of how long pre-catalysts have to be pretreated under hydrogen yielding solvate complexes to exclude any induction periods.

Therefore, we developed a method applying UV/Vis spectroscopy for the quantitative determination of rate constants for the stoichiometric hydrogenation of rhodium diolefin complexes (Figure 2).

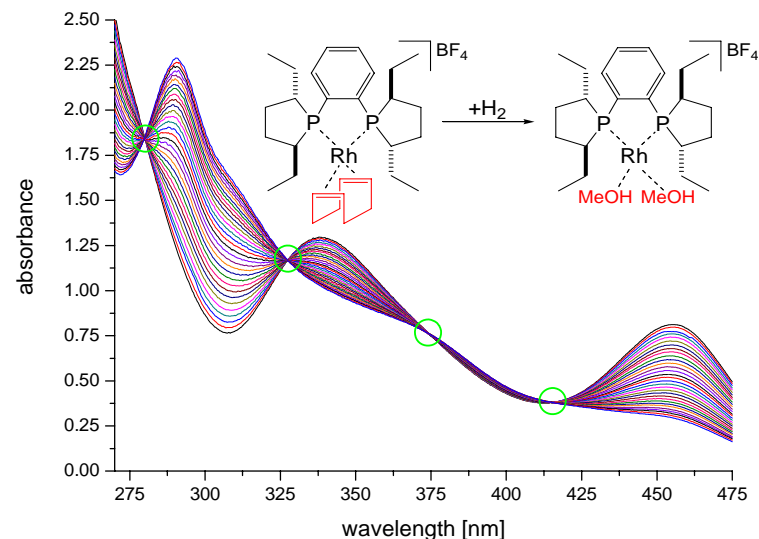


Figure 2. Stoichiometric hydrogenation of $[\text{Rh}(\text{Et-DuPHOS})(\text{COD})]\text{BF}_4$; 0,0096 mmol (7.8 mg) in 15 ml MeOH; layer thickness 0.5 cm; 60 nm/min; 25.0 °C.

References

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3. Heller, D., de Vries, A. H. M., de Vries, J. G. in "Handbook of Homogeneous Hydrogenation" (H. G. de Vries, C. Elsevier, eds.) ch. 44, p. 1483, WILEY-VCH, Weinheim, 2007.