Multinuclear rhodium complexes in asymmetric hydrogenation

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Introduction

In asymmetric hydrogenation with rhodium/diphosphine complexes, solvate complexes of the type [Rh(PP)(solvent)$_2$]anion (with PP = chiral diphosphine) are known to afford maximum activity.[1] Such solvate complexes, however, react with a variety of anions resulting in μ-anion bridged multinuclear complexes. The first example of a trinuclear rhodium complex [Rh$_3$(PP)$_3$(μ_2-X)$_2$]anion has been reported by Halpern et al. in 1977 with the achiral ligand DPPE (1,2-bis(diphenyl)phosphinoethane).[2] Complex [Rh$_3$(DPPE)$_3$(μ_2-OMe)$_2$]$^+$ had been gained by addition of NEt$_3$ to a methanolic solution of [Rh(DPPE)(MeOH)$_2$]$^+$. Similarly, the analog BINAP complex (BINAP = 2,2'-bis-(diphenyl-phosphino)-1,1'-binaphthyl) [Rh$_3$(BINAP)$_3$(μ_2-OH)$_2$]$^+$ was isolated from [Rh(BINAP)(MeOH)$_2$]$^+$ and aqueous ammonia by Saito et al.[3] Neutral μ-halogen-bridged complexes [Rh$_2$(PP)$_2$(μ_2-X)$_2$] have been used as pre-catalysts in the asymmetric hydrogenation, typically generated *in situ* from the rhodium source e.g. [Rh$_2$(cod)$_2$(μ_2-Cl)$_2$] and the chiral ligand. Few have been isolated and analyzed by X-ray.[4]

Results and Discussion

The addition of bases such as NEt$_3$ to solvate complexes can be used as a general method for synthesis of trinuclear rhodium complexes with μ-methoxy or μ-hydroxy bridge. Several trinuclear complexes have been synthesized and analyzed by X-ray, Figure 1, left.[5]

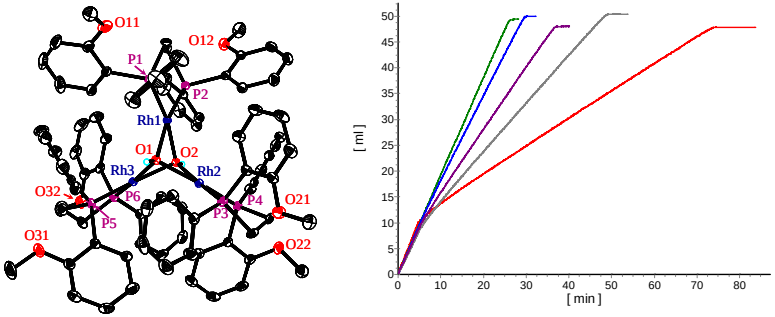

Figure 1. X-ray structure of [Rh$_3$((*S*,*S*)-DIPAMP)$_3$(OH)$_2$]$^+$, left, and asymmetric hydrogenation of methyl (*Z*)-acetamido cinnamate with [Rh(DIPAMP)(MeOH)$_2$]BF$_4$ under addition of different amounts of NEt$_3$ after 20% conversion of the prochiral olefin.

However, if bases such as NEt$_3$ or basic substrates are added to hydrogenation solutions, deactivation phenomena can occur, Figure 1, right.

Analogously, by addition of halides such as NaCl or NaBr to solvate complexes, di- and trinuclear complexes can result, Figure 2.

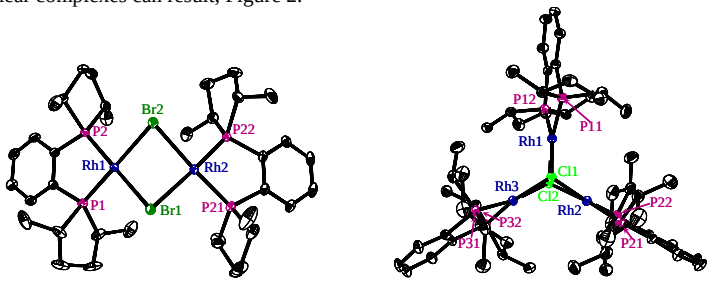

Figure 2. X-ray structure of [Rh$_2$((*S*,*S*)-Me-DuPHOS)$_2$(μ_2-Br)$_2$] and [Rh$_3$((*R*,*R*)-Me-DuPHOS)$_3$(μ_2-Cl)$_2$]$^+$.

If added to hydrogenations, in dependence on the stability of the substrate complexes formed from the solvate complex and the prochiral olefin activities decrease, eventually to a degree that the hydrogenation is completely disabled.

Significance

Trinuclear rhodium complexes with μ-methoxy or μ-hydroxy bridge, which are formed by addition of basic additives or if the substrate itself is basic enough, and di- and trinuclear rhodium complexes with μ-halogen bridge formed upon addition of halides (which may enter the system e.g. if they are not properly removed from the substrate during work-up) can lead to deactivation phenomena in the asymmetric hydrogenation with rhodium/diphosphine complexes.

References

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