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MaxPHOS Ligand: PH/NH Tautomerism and Rhodium-Catalyzed Asymmetric Hydrogenations

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Abstract: MaxPHOS is an active and robust P-stereogenic ligand for asymmetric catalysis. The presence of an –NH– bridge between the two phosphine moieties allows the NH/PH tautomerism to take place. The neutral ligand, in which the NH form predominates, is an air-sensitive compound. However, protonation of MaxPHOS leads to the stable PH form of the ligand, in which the overall positive charge is distributed on both P centers. This protonation turns the MaxPHOS·HBF_4 salt **3** into an air-stable compound both in the solid state and in solution. The salt **3** is also a convenient precursor for the preparation of rhodium(I) complexes by direct ligand exchange with the complex [Rh(acac)(cod)]. Finally, the corresponding rhodium(I)-MaxPHOS complex was tested in the asymmetric hydrogenation of a wide range of substrates. The complex proved to be a highly selective and robust system in these reactions.

Keywords: asymmetric catalysis; hydrogenation; P ligands; rhodium; tautomerism

Introduction

Chiral phosphines make a critical contribution to the achievement of high activity and selectivity in asymmetric catalysis.[1] Consequently, much research effort has been devoted to developing a wide array of efficient phosphine ligands for a range of catalytic processes. Among these, P-stereogenic electron-rich alkylphosphines are highly proficient in asymmetric hydrogenation and other industrially relevant processes.[2] A critical disadvantage of this class of compounds is that some of them are prone to oxidation when exposed to air and therefore have to be handled under a strictly inert atmosphere.[3] P-stereogenic secondary phosphine oxides (SPOs) and P-stereogenic secondary iminophosphoranes (SIPs) do not have this limitation as there is tautomeric equilibrium between the pentavalent iminophosphorane and the corresponding aminophosphane (Figure 1).[4] This equilibrium is usually shifted towards the P(V) form, which makes SPOs and SIPs stable to oxidation. However, in the presence of a metal source, coordination to the metal efficiently shifts the equilibrium towards the P(III) form. We and others have shown that SIPs are configurationally stable through the PH/NH tauto-

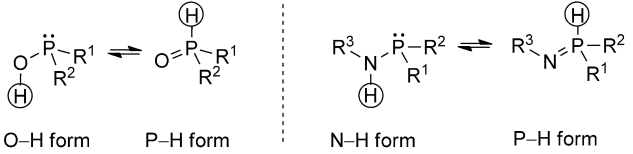

Figure 1. Phosphinous acid/SPO tautomerism (*left*) and aminophosphine/SIP tautomerism (*right*).