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Nickel(II) and Palladium(II) Complexes of the Small-Bite-Angle P-Stereogenic Diphosphine Ligand MaxPHOS and Its Monosulfide

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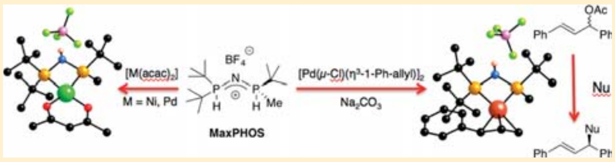
Supporting Information



ABSTRACT: Coordination studies of the optically pure diphosphine ligand (t-Bu)$_2$P(NH)P(t-BuMe) (MaxPHOS) and its monosulfide with several Pd and Ni moieties are described. Treatment of a solution of MaxPHOS·HBF$_4$ with [M(acac)$_2$] (M = Ni, Pd) in methanol or dichloromethane cleanly produced [M(MaxPHOS)(acac)]BF$_4$. Reaction of the same salt with Pd(OAc)$_2$ in the presence of excess NaBr in methanol produced the corresponding neutral complex [PdBr$_2$(MaxPHOS)]. The [PdCl$_2$(MaxPHOS)] complex was prepared by the reaction of free (S)-MaxPHOS with [PdCl$_2$(cod)]. Reaction of (S)-MaxPHOS·HBF$_4$ with Pd allylic dimers [PdCl(η^3-R-C$_3$H$_4$)]$_2$ (R = 2-methyl, 1-phenyl, 1,3-diphenyl) in the presence of excess Na$_2$CO$_3$ and NH$_4$BF$_4$ in dichloromethane produced the cationic complexes [Pd(MaxPHOS)(η^3-R-allyl)]BF$_4$ in good yields. Reaction of MaxPHOS monosulfide with [Pd(acac)$_2$] produced the neutral complex [Pd(MaxPHOS·S)$_2$], where both ligands are anionic. Protonation of this complex generated [Pd(MaxPHOS·S)$_2$]BF$_4$, a complex formally bearing an anionic and a neutral ligand. Full characterization, including five crystal structure determinations, for all of the complexes is provided. Preliminary catalytic studies of the performance of the Pd allylic complex [Pd(MaxPHOS)(η^3-2-Me-allyl)]BF$_4$ in allylic substitution reactions are also presented.

INTRODUCTION

Chiral diphosphines are a critically important type of ligand in enantioselective catalysis.[1,2] Most of the reported diphosphines are chiral due to the presence of stereogenic carbon atoms in the backbone or because they contain atropoisomeric units such as 1,1-binaphthyl groups. Less frequent are those phosphines whose chirality is due to the existence of asymmetrically substituted phosphorus atoms, a family known as P-stereogenic ligands. This type of ligand has a long history in homogeneous catalysis, which can be traced back to the influential work of Knowles and co-workers with PAMP and DiPAMP in the 1970s in asymmetric hydrogenation to produce the drug L-DOPA.[3,4] Since then, newer synthetic methods based on the use of phosphine−boranes as versatile synthetic intermediates[5−7] have allowed the preparation of a new generation of P-stereogenic ligands, prompting a renaissance of the field.[8−13] Some of these new ligands, represented in Figure 1, have been found to be extremely efficient in Rh-catalyzed asymmetric hydrogenation and other catalytic reactions.[14−23]

Interestingly, many of the best ligands bear on their phosphorus atoms the bulky *tert*-butyl group and the smallest alkyl, namely the methyl group. It seems that this combination is very well suited to generate active and enantioselective Rh precursors for catalytic hydrogenation.

In 2010, Riera, Verdaguer, and co-workers contributed to the renewed interest in the application of P-stereogenic ligands in Rh-catalyzed hydrogenation with the MaxPHOS ligand (Figure 1),[18] a bulky C_1-symmetric diphosphine ligand with a NH group bridging the two P atoms, one of them carrying the t-Bu/Me combination. This ligand can be considered analogous to Hoge's trichickenfootphos (TCFP),[17] with the advantage of not requiring preparative HPLC in its synthesis. It turned out to be a very competent ligand for the hydrogenation of several substrates catalyzed by Rh complexes.[18,24,25] With the aim of exploring the potential of the MaxPHOS ligand in reactions catalyzed by other late transition metals, we present here the coordination studies of this ligand with Ni(II) and Pd(II) moieties and some preliminary catalytic results.

RESULTS AND DISCUSSION

MaxPHOS·S. The free MaxPHOS ligand is a very air-sensitive oil, which has to be handled under strict exclusion of oxygen.[26] This behavior is not surprising, due to the electron-rich character of the phosphorus atoms, which have to be protected to avoid oxidation. Accordingly, the phosphonium

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