SYNLETT Spotlight 457

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This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

6-Diphenylphosphinopyridin-2-(1H)-one (6-DPPon)

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Dedicated with best wishes to Prof. Dr. Bernhard Breit at Albert-Ludwigs-Universität Freiburg

Introduction

Among heterocyclic structural units, pyridines are the most prevalent and have attracted the attention of chemists.1 One important aspect of pyridine chemistry is designing new ligands based on the pyridine core.2 Inspired by DNA base pairing, 6-DPPon (white solid, mp: 187 °C) was introduced by Bernhard Breit (Albert-Ludwigs-Universität Freiburg) as a monodentate ligand.3 This compound can not only be easily prepared (Scheme 1) but also has a brilliant property: the ability for self-assembly.4

Scheme 1 Preparation of 6-DPPon

6-DPPon has two tautomeric forms, a 2-pyridone and a 2-hydroxypyridine tautomer (Scheme 2).

Scheme 2 Tautomeric forms of 6-DPPon

Interaction between form A and form B through hydrogen bonding can in situ generate a bidentate donor ligand in the coordination sphere of a metal (rhodium and platinum) center (Scheme 3). The present subject can open new gates to the design of self-assembled ligands and can be considered in related chemistries.

Scheme 3 Self-assembly of the 6-DPPon ligand

Abstracts

(A) Room Temperature Ambient Pressure (RTAP) Hydroformylation of Terminal Alkenes

Breit and co-workers have developed a hydroformylation of terminal alkenes under mild conditions: at room temperature and under ambient pressure. A bidentate donor ligand, generated in situ by self-assembly of 6-DPPon, reacted with rhodium and created a new catalyst with unique properties. Various ligands were tested in comparison to 6-DPPon and the best results (high yield and little isomerization) were obtained with 6-DPPon. High selectivity, low catalyst loading, a high level of generality, and excellent reactivity were some promising aspects of this protocol.5 It was found that terminal alkenes can be hydroformylated in aqueous media by slightly changing the reaction conditions. Breit and co-workers investigated various surfactants, and the results indicated that polyoxyethanyl-α-tocopheryl sebacate (PTS) was the best choice. Interestingly, 6-DPPon was the best ligand for this reaction. It is worth noting that in addition to the advantages described above, with the new protocol the structure of the self-assembly catalyst is stable in water as a protic solvent; an important point for self-assembled structures.6
(B) Tandem Rhodium-Catalyzed Hydroformylation–Hydrogenation of Alkenes

In 2012, a unique tandem reaction was designed. In this reaction, a one-pot conversion of alkenes into linear alcohols is achieved using two different transformations (hydroformylation of alkenes and aldehyde hydrogenation). The first step (hydroformylation) was mediated by a rhodium complex which was generated by coordination of two 6-DPPon’s, and a second step was carried out with an acylguanidine ligand. High regioselectivity and simultaneous a highly chemoselective reduction were two highlights of this work.7

(C) Hydroformylation of Alkynes

Alkynes were hydroformylated stereo- and chemoselectively using 6-DPPon as a self-assembling ligand. In this study, several derivatives of the mentioned ligand were designed and investigated. This was the first time that dialkyl- as well as diaryl-substituted alkynes furnished E-enals with excellent chemo- and stereoselectivity.8

(D) One-Pot C3-Homologation of Terminal Alkenes

A new method to furnish carbonyl and carboxylic compounds was established by Breit and co-workers. In this method, by a combination of regioselective RTAP hydroformylation with 6-DPPon and a rhodium catalyst followed by decarboxylative Knoevenagel reaction (organocatalysis), various interesting compounds were produced.9 In all of the reactions, the presence of 6-DPPon was crucial.

References