



Isoprene hydroamination catalyzed by palladium xantphos complexes

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ABSTRACT

Pd(II) Xantphos or Xantphos chalcogenide complexes with general formula $[PdCl_2(X\cap X)]$ (where X = P, O, S or Se) were synthesized by the addition of corresponding ligands to $[PdCl_2(COD)]$ (COD = 1,5-cyclooctadiene). Prepared Complexes $[PdCl_2(Xantphos)]$ and $[PdCl_2(Xantphos=S)]$ showed distorted square planar geometries, from X-ray crystallographic analysis. All of the prepared complexes showed activity toward intermolecular hydroamination of isoprene with a variety of secondary amines. Complete conversion (~100%) of pyrrolidine was observed using Pd–Xantphos as catalysts. Hydroamination reactions exhibited regioselectivity when crowded secondary amines were used.

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1. Introduction

Intermolecular hydroamination, the addition of N–H bond across C=C multiple bonds has recently received great deal of attention because being a 100% atom-economy process. The reaction allows direct access to a large variety of amines which are important target products or intermediates in organic and medicinal chemistry. A number of papers were published [1–10], reporting the hydroamination of alkenes or alkynes and the difference between hydroamination and related oxidative amination reactions. Hydroamination is known to be catalyzed by complexes of early/late transition metals (especially groups IX and X) and some lanthanide complexes [11–15]. The big step in hydroamination of C=C bonds took place at the start of the 21st century when Hartwig and his co-workers published intermolecular reactions of vinylarenes with arylamines using palladium–phosphine systems either with OTf[−] or in the presence of triflic or trifluoroacetic acids as co-catalysts [16]. The addition took place in anti-Markovnikov fashion and strong evidence (computational [17] and experimental [18]) supported the presence of η^3 -phenethyl palladium complex as the intermediate. Pd complexes bearing sterically hindered PXP ligands (where X = C or N) were discovered to catalyze the hydroamination of primary and secondary amines with activated alkenes [19]. Palladium diphosphine complexes were also found to catalyze the hydroamination of secondary alkyl, cycloalkyl

and benzylic amines to acrylic type alkenes [20]. Although the isolated yields were remarkable in most cases, drastic conditions were necessary for the reaction.

Hydroamination of 1,3-dienes with ammonia underlie the promising preparation procedures for higher amines. The most interesting product of butadiene hydroamination with NH₃ is tris(2,7-octadienyl)amine that can be easily hydrogenated to obtain trioctylamine, a valuable extractant extensively applied in isolation processes of a large number of noble and rare metals. In the earlier studies, butadiene hydroamination was performed in the presence of palladium catalyst with triarylphosphine or dialkylarylphosphine oxide ligands, with anhydrous ammonia under high pressure. The product distribution depends on the ratio of butadiene to ammonia and on the character of the solvent, as well as the concentration of NH₃. Hydroamination of isoprene catalyzed by Pd and Ni complexes provides a convenient synthetic method to aminoterpenes [21,22]. Since the isoprene could be coupled in four fashion (head-to-tail, tail-to-head, head-to-head, and tail-to-tail), the composition of the 2:1 adducts of isoprene and amines are usually complex. From the synthetic point of view, the importance of the procedure for the preparation of amino-substituted hemiterpenes and monoterpenes is its selectivity to prenolamine, buteneamines and 3,7-dimethylocta-2,7-dien-1-amine. These compounds are structural elements of a diverse natural isoprenoids [23] (see Scheme 1).

The main factors determining the regioselectivity in the reactions of isoprene with amines are (a) the nature of initial amine, (b) the structure of activating ligand in the catalyst, and (c) the presence of acid co-catalyst (HOTf or BF₃·Et₂O) [24]. The nature

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