

ORIGINAL PAPER

Copper hydride-catalyzed reduction of electron-deficient olefins

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Copper hydride derived from $\text{CuF}(\text{PPh}_3)_3 \cdot 2\text{MeOH}$ –bis[(2-diphenylphosphino)phenyl] ether–silane can reduce electron-deficient olefins selectively and efficiently.

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Introduction

Selective conjugate reduction of electron-deficient olefins, e.g. α,β -unsaturated carbonyl compounds, is an important transformation in organic synthesis. Versatility of this reaction has been well demonstrated in the synthesis of some molecules with complex structures (Nicolaou et al., 2005; Li et al., 2008). Although several methods can be used for this transformation (Magnus et al., 2000; Blackwell et al., 2002; Jung & Krische, 2006; Hirasawa et al., 2007; Monguchi et al., 2008), $[\text{CuHPPH}_3]_6$ has been recognized as the reagent of choice for this kind of reactions due to its high regioselectivity, mild conditions and tolerance of other functional groups including isolated $\text{C}=\text{C}$ bond (Mahoney et al., 1988; Brestensky & Stryker, 1989; Chiu, 1998; Rendler et al., 2007; Sass et al., 2011). A combination of $[\text{CuHPPH}_3]_6$ as the catalyst and other reducing reagents, e.g. Bu_3SnH (Lipshutz et al., 1998), make this reduction very attractive from the economic point of view. The use of silanes instead of tin hydrides as the reducing reagents makes this reaction economical and environmentally benign (Lipshutz et al., 2000). Employment of the $[\text{CuHPPH}_3]_6$ catalyst generated in situ from stable copper compounds and silane as the reducing reagent makes this method more feasible and practical than that using $[\text{CuHPPH}_3]_6$, as it avoids long-time storage of air-unstable $[\text{CuHPPH}_3]_6$ and its high cost. Ito (1997) reported the formation of copper hydride from CuCl

and hydrosilane in 1,3-dimethylimidazolidinon, and its application in conjugate reduction. Mori et al. (1997) reported that silanes are able to reduce enones in 1,4-selectivity in the presence of a catalytic amount of $\text{CuF}(\text{PPh}_3)_3 \cdot 2\text{EtOH}$ or $\text{CuCl-PPh}_3\text{-Bu}_4\text{NF}$ in *N,N*-dimethylacetamide (Mori et al., 1999) affording saturated ketones in high yields. However, these copper hydrides are not very reactive with bulky ketones and some latent polarized olefins. Optimization of the ligand has led to the discovery that copper hydride ligated with 1,2-bis(diphenylphosphino)benzene (DPBen, Fig. 1) is a more efficient catalyst for conjugate reduction of enones or unsaturated esters, and interestingly, more stable than $[\text{CuHPPH}_3]_6$ (Baker et al., 2008). CuH-DPBen has been used to catalyze conjugate reduction of isophorone and unsaturated esters (including thioesters) (Baker et al., 2008; Li et al., 2011; Ou et al., 2012) which are inert to $[\text{CuHPPH}_3]_6$.

Even though copper hydride is regarded as a suitable reagent/catalyst for conjugate reduction of α,β -ketones and esters, there are a number of reports showing that the choice of phosphine ligands is of great importance for the selectivity for the reduction of unsaturated carbonyls. For α,β -unsaturated aldehydes, 1,2-reduction is the predominant reaction using the copper catalyst; for α,β -unsaturated ketones, 1,4-reduction with triphenylphosphine or DPBen as the ligand occurs, whereas 1,2-reduction proceeds using some aryldialkylphosphines as the ligands (Chen, et al., 2000; Lee & Lipshutz, 2008). In most cases,

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