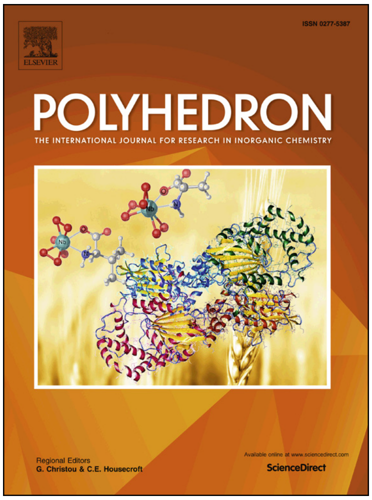

Zirconium-Catalyzed Hydroarsination with Primary Arsines

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Zirconium-Catalyzed Hydroarsination with Primary Arsines

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Keywords: Hydroarsination, zirconium, arsenic, catalysis, photocatalysis

Abstract

The zirconium compound, [κ^5-*N*,*N*,*N*,*N*,*C*-($Me_3SiNCH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2$]Zr (**1**), catalyzes the hydroarsination of alkenes with primary arsines, previously unknown substrates for this transformation. Irradiation in the ultraviolet, near-UV, or visible with commercially-available light sources are critical for this catalysis. Styrene substrates are unreactive without irradiation, but Michael acceptors give products in the dark or under irradiation with any source. These observations suggest that the zirconium arsenido intermediate engages in insertion based hydroarsination under photolysis, but the arsenido ligand is nucleophilic without photoexcitation.

Keywords: Hydroarsenation catalysis, zirconium, arsenide, photocatalysis, arsine

1. Introduction

Catalytic heterofunctionalization involving group 15 elements is a proven methodology to generate new C–E bonds for both nitrogen and phosphorus, yet catalytic hydroarsination is rare, with only a handful of reported examples of this reaction.[1-10] Nevertheless, such a strategy offers an atom-economical and direct route to organoarsines, but the transformation is limited to only a handful of substrates and often precious-metal catalysts.[2-4, 9] All reported transformations utilize secondary arsine substrates with the exception of one case that utilizes an arsenylborane.[6] Thus far, hydroarsination with primary arsines to selectively make secondary