SYNLETT Spotlight 89

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

Synthetic Applications of Tris(pentafluorophenyl)borane

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Introduction

Reactions in the presence of Lewis acids are commonplace in modern synthetic chemistry. 1 Pentafluorophenylborane compounds were first reported in the 1960s by Chambers2 and Massey but their strong Lewis acidity was unexploited until the 1980s when Paetzold and co-workers generated monomeric iminoborane which undergoes cycloaddition reactions with nitriles or isonitriles (Equation 1).3 Since then, their application in catalysis has increased tremendously.4 Tris(pentafluorophenyl)borane has emerged as a powerful but selective reagent in many organic transformations.5 Due to its uniqueness, it is a ubiquitous component of many important alkyl-based olefin polymerization catalysts and functions in non-traditional Lewis acid catalyzed reactions involving reduction of alcohols, cleavage of aryl and alkyl ethers, nonactivated aziridines6 and epoxides. Furthermore, it catalyzes hydroisilylation of aromatic aldehydes, ketones, ethers,7 and imines.8 Tris(pentafluorophenyl)borane is commercially available but various methods have been developed over the years for its preparation. One preparation involves the formation of a pentafluorophenyl metal (Group 11 or 12), followed by treatment with a boronhalide.9

Abstracts

(A) Hydrosilation of aromatic compounds catalyzed by 1–4 mol% of tris(pentafluorophenyl)borane is a mild and selective addition of Ph3SiH at room temperature. Yields and conversion rates for this transformation are high and the reactivity order is esters >> ketone > aldehyde which is paradoxical to the normal reactivity pattern.8

(B) Secondary benzylic alcohol derivatives undergo allylation with allylsilanes in the presence of catalytic amounts of B(C6F5)3. Other functionalities such as bromo, acetoxy, and primary benzyloxy groups also undergo smooth allylation.10

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(C) Reduction of imines to amines is an important organic transformation. A variety of benzaldimines and ketimines are mildly and effectively hydrosilated in good to excellent yields.11

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\begin{align*}
\text{MeO} & \quad \text{PhMe}_2\text{SiH} \quad \text{PhCH}_3 \\
\text{N} & \quad \text{Bn} \\
\text{N} & \quad \text{Bn} \\
\text{MeO} & \quad \text{PhCH}_3 \\
\text{H} & \quad \text{MeO} \\
\text{B(C}_6\text{F}_5\text{)}_3 & \quad \text{97% yield}
\end{align*}
\]

(D) Aziridine ring opening is an important organic transformation that generates versatile nitrogen building blocks found in many biological systems. Nonactivated aziridines undergo nucleophilic ring opening with catalytic amounts of B(C_6F_5)_3 to yield the corresponding trans-diamine.6

\[
\begin{align*}
\text{N} & \quad \text{Bn} \\
\text{N} & \quad \text{Bn} \\
\text{H}_2\text{N} & \quad \text{OMe} \\
\text{10 mol %} & \quad \text{B(C}_6\text{F}_5\text{)}_3 \\
\text{MeCN, 65 °C} & \quad \text{NH}_{\text{Bn}} \\
\text{99%} & \quad \text{OMe}
\end{align*}
\]

References