

## Ni-Catalyzed Multi-Component Coupling Reaction of Aldimine, 1,3-Diene, Alkyne, and Organozinc

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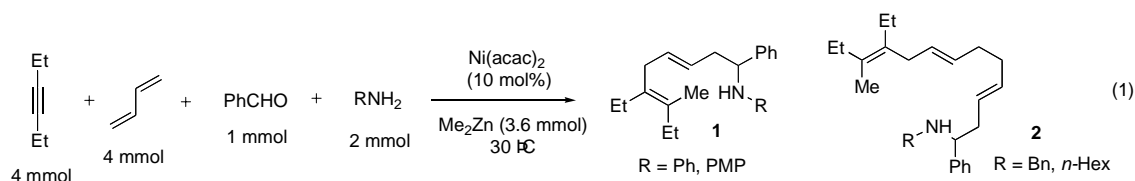
Key Words; Nickel, Organozinc, Diene, Aldehyde, Amine

### Abstract

Aldimines composed of aldehydes and primary amines react with 1,3-diene, alkyne, and Me<sub>2</sub>Zn to furnish dienyl homoallylamines in the presence of Ni catalyst. In case of Ph<sub>2</sub>Zn, alkyne serves as a spectator ligand to promote the three-component coupling reaction of Ph<sub>2</sub>Zn, diene, and aldimine.

### Introduction

In the presence of Ni(acac)<sub>2</sub> catalyst, aldimines prepared from aldehydes and amines reacted with Me<sub>2</sub>Zn, alkynes, and 1,3-butadienes to furnish dienyl homoallylamines **1** in good yields (eq 1).<sup>1</sup> Aromatic amine imines reacted with a diene-Ni complex **I** in the presence of Me<sub>2</sub>Zn to form dienylamine **1** through a nickellacycle **III** (Scheme 1). In sharp contrast to the result, aldimines composed of aldehydes and aliphatic amines selectively furnished trienyl homoallylamines **2** in excellent yields, incorporating two molecules of 1,3-butadiene. For less reactive aliphatic amine imines, **I** might not be reactive enough; hence, more reactive, less populated bis-butadiene-Ni **II** participated in the reaction to exert dienylamine **2** via allylnickel intermediate **IV**.

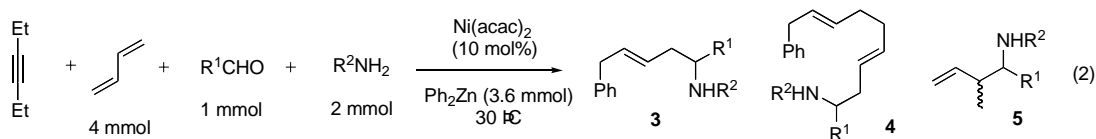


### Results and Discussions

Ph<sub>2</sub>Zn shows entirely different reactivity from Me<sub>2</sub>Zn under similar conditions (eq 2). The coupling reaction of Ph<sub>2</sub>Zn, 1,3-butadiene, aldehydes, and amines

(PMPNH<sub>2</sub> and BnNH<sub>2</sub>) was undertaken in the absence or in the presence of 3-hexyne at 30 °C within several hours (Table 1). The reaction mechanism for the Ni-catalyzed multi-component coupling reaction with Ph<sub>2</sub>Zn is also displayed in Scheme 1. In all cases, 3-hexyne is not incorporated in the products at all and serves as a spectator ligand controlling the selectivities.

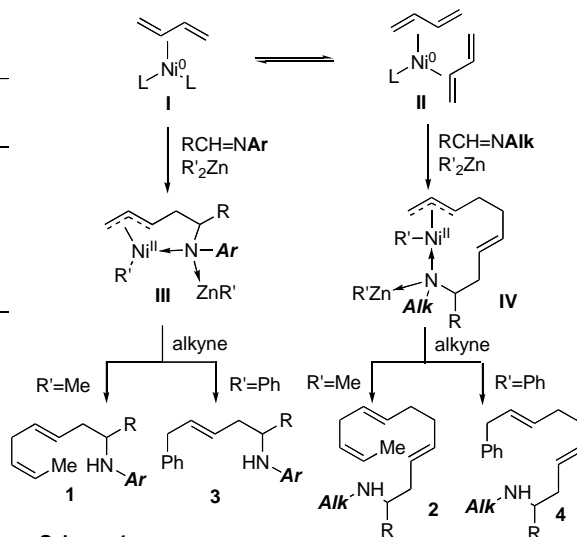
In the absence of 3-hexyne, a mixture of the coupling product **3**, dienylamine **4**, and homoallylamine **5** was obtained (run 1, Table 1). Interestingly, 3-hexyne is essential for the selective formation of **3** or **4**. In the presence of 1 mmol of 3-hexyne, aldimine prepared from aromatic amine (PMPNH<sub>2</sub>) and benzaldehyde reacts with Ph<sub>2</sub>Zn and 1,3-butadiene in a 1:1:1 ratio to provide homoallylamine **3** in high yield along with a slight amount of **4** (run 2). Four equivalents of alkyne show excellent selectivity to produce homoallylamine **3** as a single product, preventing the formation of **4** and **5** (run 3). Aliphatic aldehydes showed somewhat diminished reactivity and reduced yields, yet provided the expected products in acceptable yields (runs 4 and 5). On the other hand, aliphatic amine reacts with Ph<sub>2</sub>Zn and butadiene in a 1:1:2 ratio to furnish dienyl homoallylamine **4** exclusively, irrespective of the kinds of aldehydes (runs 6 and 7).



**Table 1.** Ni-Catalyzed Multi-component Coupling Reaction with Butadiene, Aldimine, and Ph<sub>2</sub>Zn in the presence of 3-Hexyne

run	R <sup>1</sup>	R <sup>2</sup>	alkyne (mmol)	time (h)	isolated yield		
					<b>3</b>	<b>4</b>	<b>5</b>
1	Ph	PMP	0	1	27	29	42
2	Ph	PMP	1	3	85	8	0
3	Ph	PMP	4	3	81	0	0
4	<i>n</i> -Pent	PMP	4	6	65	0	0
5	<i>c</i> -Hex	PMP	4	6	71	0	0
6	Ph	Bn	4	6	0	94	0
7	<i>n</i> -Pent	Bn	4	6	0	63	0

PMP; *p*-Methoxyphenyl



**Scheme 1**  
Contrasting Reactivity of Ph<sub>2</sub>Zn and Me<sub>2</sub>Zn for the Ni-Catalyzed Multi-component Connection Reaction

## Reference

1. M. Kimura, Y. Tatsuyama, Y. Tamaru et al., *J. Am. Chem. Soc.*, **128**, 6332, (2006).