



# Theoretical and experimental study of the nickel-catalyzed isomerization of 2-Methyl-3-butenitrile and the effect of a Lewis acid

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## ABSTRACT

A combined experimental and theoretical study was conducted to investigate the isomerization of 2-methyl-3-butenitrile (2M3BN) to 3-pentenitrile (3PN) and to 2-methyl-2-butenitrile (2M2BN) catalyzed by nickel diphosphine complexes. Ni(1,4-bis(diphenylphosphino)butane) (dppb) was identified as the most reactive catalyst among the complexes that we examined experimentally. Quantum mechanics (density functional theory) was then used to study the two isomerization mechanisms catalyzed by this complex. We find that for the 2M3BN  $\rightarrow$  3PN isomerization, the reaction is initiated with C–CN bond cleavage, followed by an allyl direct rotation and C–CN bond reformation. For the 2M3BN  $\rightarrow$  2M2BN isomerization, the most energetically favorable pathway begins with C–H bond activation, followed by a  $\pi$ - $\sigma$ - $\sigma$ - $\pi$  allyl rearrangement and C–H bond reformation. Our proposed mechanism for the 2M3BN  $\rightarrow$  2M2BN isomerization is slightly different (yet energetically more favorable) than that described in previous studies, where it has been suggested that 2M2BN is obtained through a  $\pi$ - $\sigma$ - $\sigma$  allyl rearrangement rather than a  $\pi$ - $\sigma$ - $\sigma$ - $\pi$  type rearrangement. Additionally, we investigated the effect of Lewis acids in the 2M3BN  $\rightarrow$  3PN isomerization, which has been shown in most experiments to attenuate the reaction. Notably, our calculations indicated that ZnCl<sub>2</sub>, which is used as a model Lewis acid, actually reduces the barriers for all elementary steps. However, the effective kinetic barrier for the isomerization increases from 23.7 (without ZnCl<sub>2</sub>) to 24.0 kcal/mol because of the formation of a very stable Ni( $\pi$ -allyl) (CN–ZnCl<sub>2</sub>) intermediate, causing a decrease in the reaction rate. This theoretical result was further confirmed by our own experiments.

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## 1. Introduction

Nickel-catalyzed hydrocyanation of 1,3-butadiene to produce adiponitrile (ADN), an important building block for nylon-6,6 production, is one of the most successful industrial homogeneous catalytic processes [1]. The process is comprised of three steps and uses Ni<sup>0</sup> complexes as the catalysts [2,3]. During the catalysis, HCN is first added to 1,3-butadiene, leading to the formation of the desired linear 3-pentenitrile (3PN) and an unwanted branched 2-methyl-3-butenitrile (2M3BN, Scheme 1(a)). In the presence of a Lewis acid as a co-catalyst, 3PN is isomerized to 4-pentenitrile and then hydrocyanated to generate ADN (c). The formation of

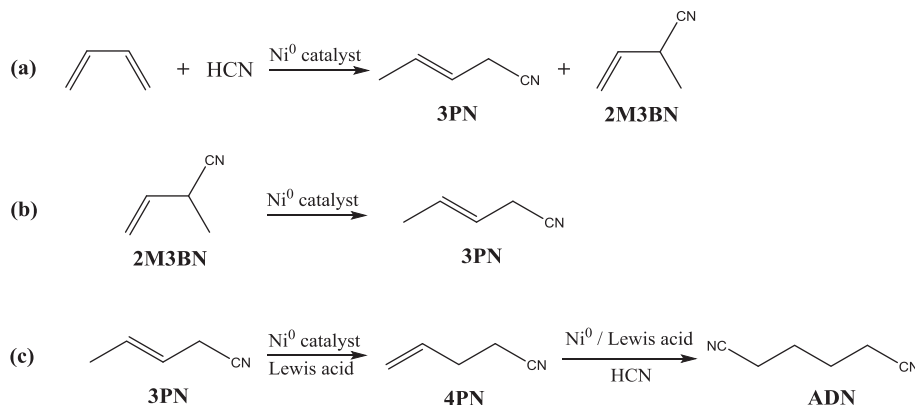
2M3BN is a negative consequence of this catalytic procedure because its direct hydrocyanation does not lead to ADN. Fortunately, 2M3BN can be isomerized to 3PN (b), which is catalyzed by the same Ni<sup>0</sup> complexes, making the entire process economically viable [4].

Numerous experimental efforts have been devoted to improve the performance of the nickel catalysts in the isomerization of 2M3BN [4–20]. Vogt et al. have synthesized a triptycene-based diphosphine ligand and found that the corresponding Ni<sup>0</sup> diphosphine catalyst has a high selectivity of 97% for the isomerization of 2M3BN to 3PN [6]. Acosta-Ramírez et al. utilized a Ni(dppf) complex (dppf = bis-diphenylphosphinoferrocene) for the isomerization, obtaining a yield of 83% for 3PN [7,8]. Hoffman and co-workers used the combination of Ni(COD)<sub>2</sub> (COD = 1,5-cyclooctadiene) and octyltriptyphos in the reaction and obtained 3PN with 93.5% yield at 96.7% conversion under optimized conditions [9]. In most studies, linear 3PN was the main product, and branched 2-methyl-

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**Scheme 1.** Reaction sequence of the Dupont adiponitrile (ADN) process.

2-butenitrile (2M2BN) was one of the byproducts [10–16]. However, when Ni(dcype) and Ni(dtbpe) (dcype = 1,2-bis(dicyclohexylphosphino)ethane and dtbpe = 1,2-bis(di-tert-butylphosphino)ethane) were used to catalyze the reaction, 2M2BN became the major product [17].

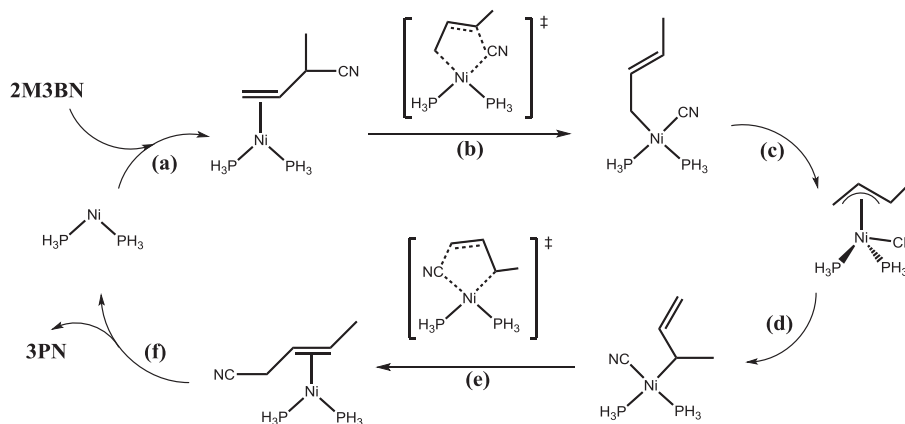
Several theoretical studies have been conducted to provide insights into the reaction mechanism [9,21,22]. Chaumonnot et al. used density functional theory (DFT) to investigate the reaction catalyzed by a Ni(PH<sub>3</sub>)<sub>2</sub> complex [21]. They proposed a reaction mechanism in which 2M3BN first forms an η<sup>2</sup>-olefin complex with Ni(PH<sub>3</sub>)<sub>2</sub> (Scheme 2 (a)). Then, C–CN is cleaved, leading to the formation of a Ni<sup>+</sup>(CN) (σ-allyl) complex (b), after which an allyl σ-π-σ rearrangement occurs ((c) and (d)). Finally, 3PN is produced through C–CN reformation (e). The problem of this DFT study is that only the thermodynamics were considered and the kinetics were completely ignored.

Jones and co-workers used a Ni(dmpe) catalyst (dmpe = 1,2-bis(dimethylphosphino)ethane) to conduct a more thorough DFT mechanistic study (considering both the thermodynamics and kinetics) of the same reaction [22]. In addition to the main pathway 2M3BN → 3PN, the 2M3BN → 2M2BN isomerization was also investigated (Scheme 3). These authors found that both isomerization reactions begin with the same η<sup>2</sup>-olefin Ni<sup>0</sup> complex, but the subsequent steps are very different. For the 2M3BN → 3PN isomerization, C–CN cleavage occurs first (a), leading to the formation of the Ni(CN) (π-allyl) intermediate. This is followed by the direct rotation of the allyl (b) instead of the allyl σ-π-σ rearrangement. The C–CN bond is then reformed, leading to 3PN (c). However, for

the 2M3BN → 3PN isomerization, it is the C–H bond that is cleaved in the beginning of the reaction to form a Ni hydride π-allyl intermediate (d). Next, allyl is rearranged through a π-σ-σ allyl rearrangement ((e) and (f)) rather than the allyl direct rotation or π-σ-σ rearrangement. Finally, 2M2BN is formed through the formation of the C–H bond (g).

Experimentally, it was found that Lewis acids affect the isomerization of 2M3BN → 3PN [3,7–10,23]. Tolman and co-workers have shown that the addition of Lewis acids (e.g., ZnCl<sub>2</sub>) facilitates the reaction, where monophosphite is used as the ligands [3]. However, some experimental studies (with Ni diphosphine complexes as the catalysts) show that the addition of Lewis acids actually decreases the rate of catalysis [7–9]. It was also found that this leads to the formation of very stable π-allyl nickel cyanide complexes that can be trapped and isolated [7–9,18]. For example, Acosta-Ramírez et al. have used Ni(dppf) to catalyze the isomerization [7]. They found that the reaction reaches 79% conversion and 67% yield to 3PN in 1 h. However, no conversion was observed after 1 h when ZnCl<sub>2</sub> was added, and the yield to 3PN was only 54% after 5 h. Hoffman and co-workers used Ni octyltrityphos complexes as the catalysts and found that the reaction rate decreases significantly in the presence of ZnCl<sub>2</sub>; for instance, the conversion of 2M3BN decreases from 95% to 8% in 1 h [9]. A μ<sub>2</sub>-chloro-bridged dimer [(P<sub>1</sub>P)Ni(η<sup>3</sup>-C<sub>4</sub>H<sub>7</sub>)CN–ZnCl<sub>2</sub>]<sub>2</sub> (P<sub>1</sub>P = 1,8-Bis(diphenylphosphino)-9,10-ethano-9,10-dihydroanthracene) was isolated and characterized.

In this work, we conducted a combined theoretical and experimental study of the isomerization of 2M3BN to the major product



**Scheme 2.** Proposed mechanism for the 2M3BN → 3PN isomerization [21].

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