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Theoretical and experimental study of the nickel-catalyzed isomerization of 2-Methyl-3-butenenitrile 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 2methyl-3-butenenitrile (2M3BN) to 3-pentenenitrile (3PN) and to 2-methyl-2-butenenitrile (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 π - σ - π -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 π - σ - σ allyl rearrangement rather than a π - σ - σ - π 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 ZnCl₂, 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 ZnCl₂) to 24.0 kcal/mol because of the formation of a very stable Ni(π -allyl) (CN–ZnCl₂) 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 Ni⁰ 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-pentenenitrile (3PN) and an unwanted branched 2-methyl-3-butenenitrile (2M3BN, Scheme 1(a)). In the presence of a Lewis acid as a co-catalyst, 3PN is isomerized to 4-pentenenitrile 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^0 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 Ni⁰ 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)₂ (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-butenenitrile (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(PH₃)₂ complex [21]. They proposed a reaction mechanism in which 2M3BN first forms an η^2 -olefin complex with Ni(PH₃)₂ (Scheme 2 (a)). Then, C–CN is cleaved, leading to the formation of a Ni⁺²(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 = 1,2bis(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 \rightarrow 3PN, the 2M3BN \rightarrow 2M2BN isomerization was also investigated (Scheme 3). These authors found that both isomerization reactions begin with the same η^2 -olefin Ni⁰ complex, but the subsequent steps are very different. For the 2M3BN \rightarrow 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 \rightarrow 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 σ - π - 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 \rightarrow 3PN [3,7–10,23]. Tolman and co-workers have shown that the addition of Lewis acids (e.g., ZnCl₂) 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 ZnCl₂ was added, and the yield to 3PN was only 54% after 5 h. Hoffman and co-workers used Ni octyltriptyphos complexes as the catalysts and found that the reaction rate decreases significantly in the presence of ZnCl₂; for instance, the conversion of 2M3BN decreases from 95% to 8% in 1 h [9]. A µ2-chloro-bridged $[(P \cap P)Ni(\eta^3 - C_4H_7)CN - ZnCl_2]_2$ dimer (P∩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 \rightarrow 3PN isomerization [21].



Scheme 3. Proposed mechanisms for the 2M3BN \rightarrow 3PN and 2M3BN \rightarrow 2M2BN isomerizations [22]. During steps (a), (b), and (c), one of the phosphorous atoms dissociated from Ni.

3PN and to the side product 2M2BN. There are two goals of this work. The first goal is to revisit the reaction mechanisms for 2M3BN \rightarrow 3PN and 2M3BN \rightarrow 2M2BN. We are particularly interested in the allyl rearrangement process. A previous theoretical study proposed that allyl rearrangement proceeds via an allyl direct rotation for 2M3BN \rightarrow 3PN, whereas the rearrangement proceeds via a π - σ - σ interconversion for 2M3BN \rightarrow 2M2BN [22]. We seek to understand what causes the change of the pathway for this particular step. The second, more significant, goal of this work is to understand the role that Lewis acids play during the isomerization. Specifically, we studied how Lewis acids affect each elementary step and what causes the decrease in the overall reaction rate.

The remainder of this paper is organized as follows. In Section 2, we detail the computational and experimental procedures. Our results are presented in Section 3, beginning with the mechanistic studies for the 2M3BN \rightarrow 3PN and 2M3BN \rightarrow 2M2BN isomerizations, followed by a discussion of the changes to the allyl rearrangement pathway. In the final section, we report how Lewis acids affect each elementary step for the isomerization and provide a rationalization for why they cause the reaction to slow.

2. Computational and experimental details

2.1. Computational details

The geometry optimizations and calculations of the zero-point vibrational energies (ZPVEs) were performed using the B3LYP functional [24] with the 6-31 + G(d) basis set for Ni and Zn, the 6-311 + G(2d,p) basis set for N, O, P and Cl, and the 6-31G(d,p) basis



Fig. 1. Selected diphosphine ligands $(Ph)_2P(CH_2)_xP(Ph)_2\ (X=1,\ 2,\ 3,\ 4,\ 5,\ 6)$ for the experimental investigation.

set for C and H. Optimized structures were verified by the calculated vibrational frequencies. No imaginary frequencies were found for the optimized structures that correspond to local minima on the potential energy surface, whereas every transition state has one imaginary frequency that corresponded to the eigenvector along the reaction pathway. Moreover, intrinsic reaction coordinate (IRC) calculations were performed to confirm that the transition states indeed connect two corresponding minima [25].

Solvation energies (G_{Sol}) were calculated using the SMD solvation model [26] implemented in Gaussian 09 [27] to represent toluene (dielectric constant = 2.3741). The solvation calculations were based on the gas-phase optimized structures. All energies discussed in this work are Gibbs free energies, calculated as

$$G_{298K} = E_{elec} + ZPVE + \sum_{\nu} \frac{h\nu}{e^{h\nu/kT} - 1} + \frac{n}{2}kT - T(S_{\nu ib} + S_{rot} + S_{trans}) + G_{solv}$$

where n = 8 for nonlinear molecules and n = 7 for linear molecules, and S_{vib}, S_{rot}, and S_{trans} are the calculated vibrational, rotational, and translational entropies.

2.2. Experimental details

General methods. All of the reactions were performed with standard Schlenk and glovebox techniques under dry nitrogen. All of the phosphine ligands, Ni(COD)₂, 2M3BN, and other chemicals used in the experiments were reagent grade, purchased from J&K and Aladdin. Toluene was dried and distilled from sodium/ benzophenone ketyl solution prior to use. Gas chromatography was performed on a SHIMADZU GC-14B chromatograph equipped with a Kromat KB-1 column (30 m-0.53 mm-2.0 μ m) and an FID detector.

Isomerization of 2M3BN using Ni(COD)₂ and diphosphine ligands. Toluene (2 mL) was added to a Schlenk tube containing Ni(COD)₂ (0.020 mmol, 1 equiv.) and the diphosphine ligands (dppm, dppe, dppp, dppb, dpppe or dpph, 0.026 mmol, 1.3 equiv.). The solution was stirred for 20 min at ambient temperature and then heated at 100 °C. 2M3BN (200 μ L, 100 equiv.) was added using an Eppendorf pipette, followed by 50 μ L of n-decane as an internal standard. Samples were taken at set times for GC analysis.

Isomerization of 2M3BN using Ni(COD)₂, dppb and ZnCl₂. Toluene (2 mL) was added to a Schlenk tube containing Ni(COD)₂ (0.020 mmol, 1 equiv.), dppb (0.026 mmol, 1.3 equiv.) and ZnCl₂ (0.026 mmol, 1.3 equiv.). The solution was stirred for 20 min at ambient temperature and then heated at 100 °C. 2M3BN (200 μ L,



Fig. 2. Conversion of 2M3BN [%] in the isomerization reaction versus number of carbon atoms between two P atoms in the ligands: dppm, dppe, dppp, dppb, dpppe and dpph. Conversion is determined by GC. 2M3BN: Ni: $L_D = 100: 1: 1.3; T = 100 \degree C; t = 2 h.$

100 equiv.) was added using an Eppendorf pipette, followed by 50 μL of n-decane as an internal standard. Samples were taken at set times for GC analysis.

3. Results and discussion

3.1. Experimental identification of highly reactive, selective nickel diphosphine complexes

We first performed a series of experiments in which diphosphine ligands with two phosphorus atoms separated by a different number of carbon atoms (i.e., $(Ph)_2P(CH_2)_XP(Ph)_2$, X = 1 (dppm), 2 (dppe), 3 (dppp), 4 (dppb), 5 (dpppe), and 6 (dpph)) were used with Ni(COD)₂ to catalyze the isomerization of 2M3BN (Fig. 1). The goal

of these experiments is to determine which nickel diphosphine complex gives the highest reactivity.

We found that dppb outperformed the other diphosphine ligands with a TOF of 48.0 h⁻¹ in 2 h, $(0.3 h^{-1} \text{ for dppm}, 0.2 h^{-1} \text{ for dppp}, 0.5 h^{-1}$ for dppp, 42.9 h⁻¹ for dpppe, and 25.7 h⁻¹ for dpph, Fig. 2). This ligand has a 2M3BN conversion of 95.9% and selectivity to 3PN of 87.8%. We note that Chaumonnot et al. reported similar results based on the same catalyst (96% conversion, 90% yield for 3PN in 3 h at 100 °C) [21]. This result motivated us to conduct a quantum mechanics study to investigate the reaction mechanism for the 2M3BN to 3PN isomerization catalyzed by Ni(dmpb) (dmpb, 1,4-bis(dimethylphosphino)butane), where the four phenyl moieties in dppb were replaced by methyl to reduce the computational cost. Additionally, we also investigated the 2M3BN isomerization to 2M2BN, the major byproduct of the 2M3BN isomerization (selectivity < 2%).

A previous DFT study has investigated the isomerization of 2M3BN to 3PN and 2M2BN catalyzed by Ni(dmpe) and provided detailed reaction mechanisms [22]. The same study also investigated the two isomerization reactions catalyzed by Ni(dmpb). However, only the initial C–CN and C–H cleavage steps were studied, and the other steps such as the allyl rearrangement and the C–CN and C–H bond formations were ignored. It should be noted that we only considered the mechanism leading to *trans*-3PN and *E*-2M2BN in this work and did not consider the mechanisms leading to *cis*-3PN and *Z*-2M2BN. This is because most of the experiments have shown that *trans*-3PN is the major product for the 2M3BN \rightarrow 3PN isomerization and *E*-2M2BN is the major product for the 2M3BN \rightarrow 2M2BN isomerization [9,12–17].

3.2. Reaction mechanism study

3.2.1. 2M3BN \rightarrow 3PN isomerization

We expected that dmpb and 2M3BN exchange with two Nibound 1,5-cyclooctadiene ligands to form a Ni η^2 -olefin diphosphine complex 1 (Figs. 3 and 4). Such an η^2 -olefin complex has been



Fig. 3. Free energy profiles for the nickel-catalyzed isomerization of 2M3BN leading to *trans*-3PN using dmpb as a ligand (kcal/mol, relative to the total energies of the separated species [Ni(COD)₂], 2M3BN, and the free ligand). Intermediate **1** can rotate its C^2-C^3 bond to form another η^2 -olefin complex (Intermediate **7** in Fig. 5) that is 1.5 kcal/mol more stable. This increases the effective barrier for the C–CN activation step from 21.4 to 22.9 kcal/mol.



Fig. 4. Selected optimized geometries for the intermediates and transition states in the $2M3BN \rightarrow 3PN$ isomerization. The unit for bond distances is Å. The color code is green for Ni, orange for P, blue for N, and grey for C. All hydrogen atoms have been omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

observed experimentally using NMR and IR spectroscopies [17,28–30]. Correspondingly, our quantum mechanics calculations show that this ligand exchange reaction stabilizes the Gibbs free energy of the system by 15.7 kcal/mol. We note that the Ni metal center adopts a square planar geometry.

Next, C–CN cleavage occurs through the transition state **1,2-TS** to form the π -allyl complex **2**, in which the metal center adopts a tetrahedral geometry. The kinetic barrier (ΔG_a) and reaction energy (ΔG) for this step are 20.4 and –4.0 kcal/mol, respectively, which is

similar to the values reported by Jones and co-workers using Ni(dmpe) as the catalyst ($\Delta G_a = 21.1 \text{ kcal/mol}$, $\Delta G = -2.2 \text{ kcal/mol}$) [19]. In **1,2-TS**, the bond distance between C² and CN (R (C²–CN)) is 1.84 Å, which is much longer than the analogous bond distance in **1** (1.47 Å), and R (Ni–CN) is 1.91 Å, which is only slightly longer than the analogous bond distance in **2** (1.89 Å). Unlike what was observed for the Ni(dmpe) case, the two Ni–P bonds remain intact during the C–CN cleavage. Specifically, the Ni–P bond distances are 2.20 and 2.20 Å for **1**, 2.20 and 2.28 Å for **1,2-TS**, and 2.26 and 2.35 Å



Fig. 5. Free energy profiles for the nickel-catalyzed isomerization of 2M3BN leading to *E*-2M2BN using dmpb as a ligand (kcal/mol, relative to the total energies of the separated species [Ni(COD)₂], 2M3BN, and the free ligand).

for **2**. This indicates that the longer four-carbon linker in dppb or dmpb is more flexible and is able to adopt itself to the more crowded environment around Ni without dissociating one of its Ni–P bonds. This may be the reason why Ni(dppb) is a better catalyst than Ni(dppe) in terms of selectivity and reactivity [22]. In intermediate **2**, R (Ni–C²), R (Ni–C³), and R (Ni–C⁴) are 2.18, 2.03, and 2.04 Å, respectively, which are similar to those in the experimentally determined structure for the analogous complex Ni(π -methylallyl) (CN) (dppb) (2.13, 1.97, and 2.06 Å, respectively) [21].

CN and C⁴ are located at opposite sites of the P–Ni–P plane in intermediate **2**. Therefore, the π -allyl group must be rotated to bind CN with C⁴. We find that this can be achieved through two pathways: a one-step allyl direct rotation ($\mathbf{2} \rightarrow \mathbf{2},\mathbf{3}$ -TS $\rightarrow \mathbf{3}$) and a stepwise allyl π - σ - σ - π rearrangement ($\mathbf{2} \rightarrow \mathbf{2},\mathbf{4}$ -TS $\rightarrow \mathbf{4} \rightarrow \mathbf{4},\mathbf{5}$ -TS $\rightarrow \mathbf{5} \rightarrow \mathbf{5},\mathbf{3}$ -TS $\rightarrow \mathbf{3}$). For the allyl direct rotation pathway, the entire C⁴–C³–C²–C⁵ chain rotates by ~180° using the Ni–C³ bond as the axis. In the corresponding transition state ($\mathbf{2},\mathbf{3}$ -TS), the chain becomes parallel to the P–Ni–P plane. ΔG_a is only 12.1 kcal/mol, suggesting that it is surmountable even at room temperature, and ΔG is endergonic by 4.6 kcal/mol. Notably, we find that R (Ni–CN) first increases from 1.89 Å to 2.07 Å and then decreases to 1.88 Å during the course of the rotation.

For the π - σ - σ - π allyl rearrangement pathway, the π -allyl moiety in **2** is first transferred to a σ -form (**4**) by forming a σ -bond between its C² and Ni by way of **2,4-TS**. The ΔG_a is 16.8 kcal/mol, which is 4.7 kcal/mol higher than that for the direct rotation pathway ($\Delta G_a = 12.1$ kcal/mol), and the ΔG is endergonic by 15.3 kcal/mol. Subsequently, intermediate **4** is transferred to another σ -allyl complex **5** through the transition state **4,5-TS**. During the process, the bond distance between C² and Ni increases (2.20 Å for **4**, 2.33 Å for **4,5-TS**, and 3.47 Å for **5**), whereas the distance between C⁴ and Ni decreases (3.61 Å for **4**, 2.31 Å for **4,5-TS**, and 1.99 Å for **5**). Finally, the allyl group eventually σ -binds with Ni through its C⁴. The ΔG_a is 23.9 kcal/mol and ΔG is -9.3 kcal/mol. This step is followed by a transformation of the σ -allyl complex **5** to another π -allyl intermediate **3** through **5,3-TS**. This step is very facile with a ΔG_a of only 2.5 kcal/mol and $\Delta G = -1.4$ kcal/mol. Referenced to intermediate **2**, the starting point of this stepwise allyl rearrangement pathway, the kinetic barrier is 39.2 kcal/mol. This barrier is much higher than that for the direct rotation pathway, suggesting that this allyl π - σ - σ - π rearrangement is unlike to be operative in catalysis.

Finally, C–CN bond formation from intermediate **3**, which occurs via **3,6-TS**, leads to the formation of the (dmpb)Ni(η^2 -3PN) complex **6**. The barrier is 19.1 kcal/mol, and the reaction free energy is exergonic by 1.2 kcal/mol. In the transition state **3,6-TS**, R (Ni–CN) is 1.91 Å and R (C⁴–CN) is 1.80 Å. Compared to the results from the previous DFT study based on Ni(dmpe) ($\Delta G_a = 23.7$ kcal/mol and $\Delta G = 1.2$ kcal/mol) [22], we find that the C–CN bond formation step catalyzed by Ni(dmpb) is kinetically more facile and thermodynamically more favorable.

Based on our calculations, we find that the most energetically favorable pathway is $1 \rightarrow 1,2$ -TS $\rightarrow 2 \rightarrow 2,3$ -TS $\rightarrow 3 \rightarrow 3,6$ -TS $\rightarrow 6$ for the 2M3BN \rightarrow 3PN isomerization, which is similar to the results from a previous study [22]. The overall reaction free energy is exergonic by just 0.6 kcal/mol and the rate determining step is $1 \rightarrow 1,2$ -TS $\rightarrow 2$, with an effective kinetic barrier of only 21.4 kcal/mol (using the most stable intermediate **2** as the reference). This suggests that this is a facile and reversible reaction, which is consistent with experimental observations [12,18].

3.2.2. $2M3BN \rightarrow 2M2BN$ isomerization

In contrast to the 2M3BN \rightarrow 3PN conversion, the isomerization of 2M3BN to 2M2BN is initiated by C–H cleavage rather than C–CN activation [28]. In the η^2 -olefin complex **1**, Ni and the migrating H bound with C² are at the opposite sites of the C⁴–C³–C² plane. Therefore, the rotation of the C³–C² bond is necessary prior to C–H activation. This leads to a slightly more stable intermediate **7** ($\Delta G = -1.5$ kcal/mol), in which the migrating H and Ni atoms are in close proximity to each other (Figs. 5 and 6). We did not calculate



7

7,8-TS

8



8,9-TS



8,10-TS





Fig. 6. Selected optimized geometries for the intermediates and transition states in the 2M3BN \rightarrow 2M2BN isomerizations. The unit for bond distances is Å. The color code is green for Ni, orange for P, blue for N, grey for C, and white for H. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Scheme 4. The effect of the CN group on the π -allyl direct rotation pathway.

the kinetic barrier because this σ -bond rotation is expected to be facile.

This step is followed by C²–H activation by Ni, leading to the formation of the π -allyl hydride intermediate **8** via the transition state **7,8-TS** with a ΔG_a of 27.8 kcal/mol. Compared to the C–CN cleavage ($\Delta G_a = 21.4$ kcal/mol), this barrier is 6.4 kcal/mol higher in energy, suggesting that C–H cleavage is not as competitive as C–CN cleavage, which is consistent with the experiments [21]. In the transition state **7,8-TS**, R (Ni–H) and R (C²–H) are 1.49 and 1.68 Å, respectively. The reaction free energy is endergonic by 18.9 kcal/mol, suggesting the Ni hydride π -allyl complex **8** is thermodynamically unstable and cannot be isolated or even observed experimentally, which is consistent with experimental observations [12].

Similar to the 2M3BN to 3PN isomerization, the hydride and C⁴ are at the opposite sides of the P–Ni–P plane in intermediate **8**. Therefore, the allyl group must rotate by ~180° to bind hydride with C⁴. Like the 2M3BN \rightarrow 3PN case, this can also be achieved through two pathways: an allyl direct rotation and a π - σ - σ - π allyl rearrangement. Our calculations show that the direct rotation pathway possesses a ΔG_a of 24.8 kcal/mol, suggesting that this process is much more difficult than that in 2M3BN \rightarrow 3PN ($\Delta G_a = 12.1$ kcal/mol). In the course of the **8** \rightarrow **8,9-TS** \rightarrow **9** transition, R (Ni–H) first increases from 1.47 to 1.65 Å and then decreases to 1.46 Å, which is similar to what occurs for R (Ni–CN) in the 2M3BN \rightarrow 3PN case. The reaction free energy is slightly endergonic by 1.1 kcal/mol.

For the π - σ - σ - π allyl rearrangement pathway, the π -allyl intermediate **8** is first converted to a σ -allyl complex **10** through **8,10**-



Fig. 7. Free energy profiles of the nickel-catalyzed isomerization of 2M3BN to 3PN using dmpb as a ligand in the absence and presence of ZnCl₂ as a Lewis acid (kcal/mol).



Fig. 8. Isomerization of 2M3BN using Ni(COD)₂ and dppb in the presence and absence of ZnCl₂ at 100 $^\circ$ C. Conversion rates were determined by GC.

TS with a $\Delta G_a = 6.8$ kcal/mol and $\Delta G = 5.2$ kcal/mol. Intermediate **10** is then transferred to another σ -allyl complex **11** through **10,11-TS** with a $\Delta G_a = 6.8$ kcal/mol and $\Delta G = -9.9$ kcal/mol. Finally, the π - σ - σ - π allyl rearrangement is completed by the transformation of the σ -allyl complex **11** to the π -bonded allyl intermediate **9**. The kinetic barrier for this step is 8.7 kcal/mol, and the reaction free energy is endergonic by 5.8 kcal/mol. Using intermediate **8** as the reference, the overall barrier for the stepwise allyl π - σ - σ - π rearrangement is 12.0 kcal/mol, which is 12.8 kcal/mol more favorable than the direct rotation pathway. This is in sharp contrast to that in the 2M3BN \rightarrow 3PN isomerization, where the direct rotation is more facile.

The η^2 -2M2BN Ni complex **12** is formed by C–H bond formation from intermediate **9** through **9,12-TS**, in which the hydride migrates to C⁴. This step is kinetically very facile and thermodynamically irreversible with a ΔG_a of only 3.4 kcal/mol and a ΔG of -27.9 kcal/ mol. Jones and co-workers have proposed that the η^2 -2M2BN Ni complex is formed through C–H bond formation from the σ -allyl intermediate, similar to **11** [22]. Therefore, we investigated this pathway (**11** \rightarrow **11,12-TS** \rightarrow **12**) and find that it is slightly unfavorable ($\Delta G_a = 9.8$ kcal/mol) relative to the **11** \rightarrow **11,9-TS** \rightarrow **9** \rightarrow **9,12-TS** \rightarrow **12** pathway ($\Delta G_a = 9.2$ kcal/mol).

Based on the DFT study, we find that for the 2M3BN \rightarrow 2M2BN isomerization, the energetically most favorable pathway is $1 \rightarrow 7 \rightarrow 7,8$ -TS $\rightarrow 8 \rightarrow 8,10$ -TS $\rightarrow 10 \rightarrow 10,11$ -TS $\rightarrow 11 \rightarrow 11,9$ -TS $\rightarrow 9 \rightarrow 9,12$ -TS $\rightarrow 12$. The overall reaction free energy is exergonic by 9.4 kcal/mol and the rate-determining step is $10 \rightarrow 10,11$ -TS $\rightarrow 11$, with an effective barrier of 30.9 kcal/mol (referenced to intermediate 7). This suggests that compared to 2M3BN \rightarrow 3PN, this process is more thermodynamically irreversible and kinetically unfavorable, which is consistent with experimental observations [12,14].

3.2.3. Factors controlling π -allyl direct rotation

In the 2M3BN \rightarrow 3PN isomerization we find that the reaction barrier for the allyl direct rotation (**2** \rightarrow **2,3-TS** \rightarrow **3**) is only 12.1 kcal/mol, making it more facile than the allyl π - σ - σ - π rearrangement. However, in the 2M3BN \rightarrow 2M2BN isomerization, the barrier increases significantly to 24.8 kcal/mol (**8** \rightarrow **8,9-TS** \rightarrow **9**), making this pathway less competitive than the π - σ - σ - π rearrangement. We were curious to determine the factors that control the allyl direct rotation pathway. Therefore, one additional set of calculations were performed in which the Ni–CN bond in the $2 \rightarrow 2,3\text{-TS} \rightarrow 3$ pathway was replaced by Ni–H, (Scheme 4 (b), $13 \rightarrow 13,14\text{-TS} \rightarrow 14$). The results and its comparison with $2 \rightarrow 2,3\text{-TS} \rightarrow 3$ (a) and $8 \rightarrow 8,9\text{-TS} \rightarrow 9$ (c) are listed in Scheme 4.

We find that the replacement of Ni–CN (a) by Ni–H (b) increases ΔG_a from 12.1 to 20.5 kcal/mol. The replacement of C^2 –H (b) by C^2 –CN (c) further increases ΔG_a from 20.5 to 24.8 kcal/mol. Based on those results, we conclude that the increase of ΔG_a in **8** \rightarrow **8,9-TS** \rightarrow **9** compared to **2** \rightarrow **2,3-TS** \rightarrow **3** is caused by (1) Ni–CN being replaced by Ni–H, and (2) C^2 –H being replaced by C^2 –CN. Based on the magnitude of the increase in ΔG_a , the former cause is the major factor.

3.3. The effect of Lewis acids on the 2M3BN \rightarrow 3PN isomerization

Next, we investigated the influence of Lewis acids on the energetics of the most favorable pathways for the 2M3BN \rightarrow 3PN isomerization. A simplified three-atom ZnCl₂ was used as a model for the Lewis acid. The calculated results and the comparison with those in the absence of the Lewis acid are summarized in Fig. 7.

Notably, we find that ZnCl₂ actually reduces the barrier for all elementary steps: for C–CN bond cleavage, the barrier is significantly reduced from 21.4 to 11.1 kcal/mol; for the allyl direct rotation, it is reduced from 12.1 to 8.8 kcal/mol; and for C–CN bond formation, it is slightly reduced from 19.1 to 18.9 kcal/mol. Our calculations show that the addition of ZnCl₂ generates a very stable Ni⁺² allyl cyanide intermediate **16**, a Ni(π -allyl) (CN–ZnCl₂) complex. This explains why these Ni⁺² π -allyl cyanide complexes were observed and isolated once ZnCl₂ is added [7–9,18].

Importantly, our results show that this highly stable intermediate is the reason why the reaction rate decreases significantly. Indeed, because of the high stability of this intermediate, most molecules were trapped in this state, making the C–CN bond formation step more difficult, with an effective barrier of 24.0 kcal/mol (referenced to **16**). This number is slightly higher than that without ZnCl₂ (23.7 kcal/mol). Our experimental results show that when ZnCl₂ is added to the reaction, the 2M3BN conversion decreased from 95.1% to only 8.7% in 1 h (Fig. 8), which is qualitatively consistent with our DFT results.

4. Conclusions

We examined the isomerization of 2M3BN catalyzed by Ni⁰ diphosphine complexes through a combined experimental and theoretical study. Our experiments show that Ni(dppb) outperformed the other catalysts in terms of reactivity for this isomerization. Subsequently, quantum mechanics was used to study the reaction mechanisms for the 2M3BN \rightarrow 3PN and $2M3BN \rightarrow 2M2BN$ isomerizations catalyzed by this complex. Our results show that the two reactions were both initiated by C-CN or C-H bond cleavage and terminated with C-CN or C-H bond reformation. However, the allyl rearrangement intermediate step is very different for each isomerization. For the 2M3BN \rightarrow 3PN process, allyl rearrangement proceeds through a direct rotation, whereas it occurs via a π - σ - σ - π allyl interconversion for the $2M3BN \rightarrow 2M2BN$ isomerization. The main reason for the change of the pathway is because of the replacement of Ni-CN by Ni-H, which increases the kinetic barrier of the direct rotation by 8.4 kcal/ mol.

In addition, we investigated the influence of Lewis acids on the Gibbs free energy surface of the 2M3BN \rightarrow 3PN isomerization. Although most experiments show that Lewis acids slow down the reaction, our results showed that ZnCl₂ reduces the barriers for all elementary steps. However, we find that the effective kinetic barrier for the isomerization increases from 23.7 (without ZnCl₂) to

24.0 kcal/mol because of the formation of the very stable Ni(π -allyl) (CN–ZnCl₂) intermediate, resulting in a slow reaction. Our experiments further confirmed this computational result.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2016.08.016.

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