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Brett D. Swartz William W. Brennessel William D. Jones*

Department of Chemistry, University of Rochester, Rochester, NY 14627, USA jones@chem.rochester.edu

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Abstract Reactions of [(dippe)NiH]₂ with benzonitrile and varying concentrations of Lewis acids (primarily BPh₃ and BF₃) have shown a dramatic variation of reaction rate compared to the same reaction without Lewis acids. When less than one equivalent of Lewis acid is used, the reaction rate is as much as 100 times greater than without Lewis acid. Boron exchange was observed with less than one equivalent of Lewis acid allowing the formation of a Ni(0)– η^2 -aryl complex (observed by low-temperature NMR and calculations) to which the Lewis acid is postulated to re-coordinate as the rate-limiting step allowing the formation of a stable Ni(II) product. When one equivalent or greater of Lewis acid is used, the reaction shows dramatic inhibition even compared to the reaction without Lewis acid. Lewis acid dissociation can be considered as the rate-limiting step under these conditions. The overall work detailed herein has shown the importance of Lewis acids in the activation of benzonitriles due to the strengthening of the C-N bond allowing for increased stabilization of the products.

Key words nickel, C-C cleavage, nitriles, Lewis acids, kinetics

The activation of carbon–carbon σ -bonds has many important applications in both organic synthesis and industrial processes. Although frequently accomplished using organic substrates in systems where strain relief or aromatization act as a driving force, recent developments have shown an increasing number of organometallic reagents have successfully performed this activation via the insertion of a transition-metal center into the carbon-carbon σbond.¹ One area of recently increased study is C-C activation using alkyl and aryl nitrile substrates.^{2,3} A number of studies have utilized Ni(0)-phosphine and phosphite catalysts as an efficient method for the activation of C-CN bonds.⁴ One particular Ni-phosphine catalyst that has been studied in detail is [(dippe)NiH]₂, which is shown to produce a reactive Ni(0) fragment and has been used to activate alkyl, allyl, and aryl nitriles, including an example pro-



vided by Garcia and Jones that demonstrated a reversible activation of benzonitrile (Scheme 1, R = X).^{1c,2a-c,5,6} The reaction of $[(dippe)NiH]_2$ and benzonitrile initially forms a η^2 -Ni(0) complex1a that is converted into a Ni(II) complex 1b, reaching an equilibrium favoring **1b** (K_{eq} = 1.62). Further study incorporated the use of para-substituted benzonitriles to examine substituent effects on the equilibrium (Scheme 1).^{2b} The strongly withdrawing functional groups including CN and CF₃ were shown to drive the equilibrium very strongly toward the C-CN activated Ni(II) product while the donating groups including NH₂ and OCH₃ drive the equilibrium towards the η^2 -Ni(0) complex. This result suggested the stabilization of the negative charge on the ipso-carbon of the substituent and is supported by a large, positive ρ-value determined in a Hammett study (+6.1). Polar solvents were also found to shift the equilibrium to the right.





Lewis acids have been used industrially in conjunction with transition-metal catalysts to improve product selectivity, reaction rates, and extend catalyst lifetimes.^{3c} For example, the catalytic hydrocyanation of olefins with Ni(0)phosphite catalysts using Lewis acids was studied and showed that the Lewis acid coordinated through the nitrogen lone electron pair prior to the reaction.⁷ An additional study of nickel-catalyzed pentenenitrile hydrocyanation indicated that the presence of Lewis acids in the reaction proB. D. Swartz et al.

motes selectivity of linear products over branched products as a result of increased steric bulk produced upon coordination of the Lewis acid to the nitrile.⁸ Lewis acids were also shown to increase the rate of reductive elimination in palladium–phosphine complexes.⁹ This was thought to occur as a result of a change in charge distribution on the nitrogen and boron or aluminum following Lewis acid coordination.¹⁰ The resultant complex is more susceptible to nucleophilic attack at the nitrile carbon by the alkyl group thereby accelerating the rate of reaction, in this case reductive elimination.⁸

Other related work by Garcia et al. investigated the activation of acetonitrile by $[(dippe)NiH]_2$ in the presence of BPh₃. The results indicated that BPh₃ acted to *inhibit* the C–CN cleavage leaving only the η^2 -nitrile nickel(0) complex, possibly related to the steric demand of the BPh₃ group.^{2c} In contrast, Brunkan et al. examined the effect of BPh₃ on the competitive C–C and C–H cleavage of allyl cyanide by $[(dippe)NiH]_2$ and found that the C–CN activation of allyl cyanide was both *faster and irreversible* in the presence of BPh₃.¹¹ Nakao observed that boron and aluminum Lewis acids dramatically increased the rate of alkyne arylcyanation using aryl nitriles.¹²

The work detailed herein describes the reaction of [(dippe)NiH]₂ and benzonitrile in the presence of Lewis acids. Since the substitution of functional groups in the paraposition of the arene had significant effects on the equilibrium of the system,^{2b} it is reasonable that the coordination of a Lewis acid would be anticipated to have some effect. Additionally, a Lewis acid should act to stabilize some of the complexes involved in the reaction possibly enabling intermediates to be better observed, providing insight into the mechanistic aspects of this system. In this paper we show that the amount and type of Lewis acid does indeed dramatically affect the rate of the reaction. Specifically, excess Lewis acid inhibits the rate of C-CN cleavage by making a stable adduct that is unreactive. In contrast, use of less than one equivalent of Lewis acid results in acceleration of the rate of C-CN cleavage by allowing the Lewis acid to coordinate to an intermediate formed further along the reaction coordinate.13

Reaction of [(dippe)NiH]₂, **benzonitrile, and Lewis acids.** As described earlier,^{2b} **1a** is converted into **1b** upon heating to 54 °C over 46 hours ($t_{1/2}$ = 607 min) and forms an equilibrium mixture in THF of **1a/1b** = 1:1.6 at 54 °C.

Reaction of [(dippe)NiH]₂, benzonitrile, and 0.5 equivalent of BPh₃. A solution of [(dippe)NiH]₂ was treated with two equivalents of benzonitrile and 0.5 equivalent of BPh₃ (per Ni) in THF-d₈ at 25 °C turning the deep red solution yellowbrown with the evolution of H₂ gas. The reaction was monitored primarily through ³¹P{¹H} NMR spectroscopy (Figure 1). The initial spectrum showed two sets of doublets at δ = 81.8 and 65.3 ppm with ²J_{PP} = 41 Hz associated with the η²coordination of the Ni(0) fragment with the nitrile portion of benzonitrile and BPh₃ coordinated to the lone electron pair of the nitrogen (Figure 1, 2a). The other set of doublets was at δ = 79.9 and 67.7 ppm with ²J_{PP} = 67 Hz associated with 1a. The sample was heated to 65 °C and both sets of doublets immediately broadened indicating exchange of BPh₃ between the Ni(0)-benzonitrile complexes. Additionally, a set of doublets at δ = 85.3 and 73.9 ppm with ${}^{2}J_{PP}$ = 20 Hz associated with the C-CN activated Ni(II)-benzonitrile complex with BPh₃ coordinated to the cyano ligand (Figure 1, 2b) started to appear and increase as well as a set of doublets at δ = 81.7 and 71.2 ppm with ²*J*_{PP} = 20 Hz (**1b**). Within 13 minutes only 1a, 1b and 2b remained, indicating that all of the available BPh₃ was coordinated to **2b** since only 0.5 equivalent of BPh₃ was present. At this point, the ${}^{31}P{}^{1}H{}$ NMR spectrum showed the peaks for **1a** to sharpen, indicating that rapid BPh₃ exchange was no longer occurring. Equilibrium between 1a and 1b was established after ~3 hours.



Figure 1 NMR spectra of the reaction of [(dippe)NiH]_2, benzonitrile, and 0.5 equivalent of BPh_3 at 65 $^\circ C$

Reaction of [(dippe)NiH]₂, benzonitrile, and >1 equivalent of BPh₃. Heating to 65 °C with one or two equivalents of added BPh₃ required 6 days to reach 96% completion with one equivalent BPh₃ and was only 90% complete with two equivalents of BPh₃ after two weeks (Figure 2). Additionally, the peaks remained sharp throughout these reactions supporting the notion that BPh₃ coordinates very favorably to **1a** and **1b**. In fact, the resonances for **2b** remain sharp under all conditions, indicating that once BPh₃ coordinates forming **2b**, no significant exchange occurs. An orange, block-like crystal (for **2a**) and an orange, needle-like crystal B. D. Swartz et al.

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Figure 3 ORTEP drawing of **2a** showing 30% probability ellipsoids. Selected bond distances (Å): C1–N1 1.241(2), Ni1–N1 1.8866(14), Ni1–C1 1.8542(17), N1–B1 1.604(2). Selected angles in degrees: B1–N1–Ni1 146.1(12), N1–C1–Ni1 72.05(10), C1–N1–B1 143.37(15).

(for **2b**) suitable for X-ray diffraction were obtained and selected bond lengths and angles are provided in Figure 3 and Figure 4.¹⁴

Curiously, these data indicate that the C–CN cleavage reaction is accelerated when less than one equivalent of BPh₃ is used versus the reaction without BPh₃; however, once the concentration of BPh₃ is increased to one equivalent or greater, the reaction is strongly inhibited. These observations indicate that BPh₃ is playing multiple roles in this reaction, one that slows C–CN cleavage but another that can increase the rate of C–CN cleavage. One clear and immediate conclusion is that the coordination of BPh₃ to the nitrile lone pair in **1a** (to give **2a**) does not accelerate C–CN cleavage. A second conclusion is that **1a**, in the presence of small quantities of BPh₃ (formed via dissociation of BPh₃ from **2a**, as evidenced by broadening of the ³¹P resonances for both



Figure 4 ORTEP drawing of **2b** showing 30% probability ellipsoids. Selected bond distances (Å): C1–N1 1.153(2), Ni1–C1 1.8567(19), Ni1–C2 1.9302(17), N1–B1 1.575(2). Selected angles in degrees: Ni1–N1–C1 176.03(16), C1–Ni1–C2 89.13(7), C1–N1–B1 175.94(17).

compounds) can also interact differently to rapidly produce **2b**. A series of distribution of species plots for reactions containing several concentrations of BPh₃ is presented below in Figure 5.

Compound **2b** appears to be substantially more stable than **1b** since it is by far the major product. X-ray bond distances and IR data show significant differences supporting this notion (Table 1). A comparison of the C–N bond distance in **1a** [1.225(6) Å] vs. **2a** [1.241(2) Å] shows a slight increase with the coordination of Lewis acid, similar to what is seen for **1b** [1.148(3) Å] vs. **2b** [1.153(2) Å]. This result is in stark contrast to IR data where complex **2b** ($v_{CN} =$ 2170 cm⁻¹) showed a much stronger CN bond than **1b** ($v_{CN} =$ 2108 cm⁻¹) by 62 cm⁻¹, which follows trends observed in the formation of M–CN–LA complexes.¹⁵ The increase in stretching frequency may be attributed to the removal of electron density from C–N σ -antibonding orbitals, strengthening the C–N bond.¹⁰

However, when comparing the Ni–CN bond distances in **1b** [1.935(2) Å] and **2b** [1.8567(19) Å] a noticeable difference (\sim 0.1 Å) is observed. The decrease in Ni–CN bond dis-

Table 1	Selected Bond Distances and IR Stretches for Ni-Benzonitrile
Complex	es

Complex number	C–N distance (Å)	Ni–CN distance (Å)	v _{CN} (cm ⁻¹)
1a	1.225(6)	1.862(7)	1745
1b	1.148(3)	1.935(2)	2108
2a	1.241(2)	1.8542(17)	1755
2b	1.153(2)	1.8567(19)	2170
3a	1.2524(19)	1.8499(15)	1722
3b	_a	_a	2130

^a No crystal structure was obtained for complex **3b**.

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Figure 5 Distribution of species plots for all concentrations of BPh₃. (a) 0 equiv BPh₃, (b) 0.5 equiv BPh₃, (c) 1.0 equiv BPh₃, (d) 2.0 equiv BPh₃.

tance in the presence of a Lewis acid indicates increased π back bonding between the metal center and the ligand ultimately resulting in a stronger bond and a more stable complex as demonstrated by the strong equilibrium shift to the right.

Reaction of [(dippe)NiH]₂, benzonitrile, and 0.5 equivalent of BF₃. A solution of [(dippe)NiH]₂ was treated with two equivalents of benzonitrile and 0.5 equivalent of BF₃ in THFd₈ at 25 °C turning the deep red solution yellow-brown with the evolution of H₂ gas. The reaction was monitored primarily through ³¹P{¹H} NMR spectroscopy. The initial spectrum showed two sets of doublets associated with the Ni(0)–(η²-benzonitrile–BF₃) complex **3a** at δ = 66.3 and 59.1 ppm with ²J_{PP} = 56 Hz and another set of doublets at δ = 79.9 and 67.7 ppm with ²J_{PP} = 67 Hz associated with **1a**. A third set of doublets, associated with the Ni(II)–benzonitrile–BF₃ complex **3b** was observed even without heating at δ = 84.2 and 74.6 ppm with ²J_{PP} = 30.5 Hz (Scheme 2).



The sample was heated to 65 °C and the Ni(0) complex resonances for **3a** and **1a** showed significant broadening as observed with BPh₃. After one hour at 65 °C, **3a** disappeared and only **3b**, **1a**, and **1b** were observed. Similar results were

observed in separate experiments employing one and two equivalents of BF_3 but unlike BPh_3 , all reached completion within two hours (see Supporting Information).

Surprisingly, the BF₃ reactions occur much more rapidly than the BPh₃ reactions even when BF₃ is at one or two equivalents. Due to the presence of back bonding between the boron and fluorine, BF₃ is a weaker Lewis acid and forms a less stable complex than BPh₃.¹⁶ IR data of **3b** show a bond stretch of 2130 cm⁻¹, 22 cm⁻¹ greater than **1b** but 40 cm⁻¹ smaller than **2b** (Table 1). On the basis of these results, BF₃ is not as strong a Lewis acid as BPh₃, but is still able to coordinate strongly enough in **3b** to shift the equilibrium completely to the right.

The greater Lewis acidity of BPh₃ over BF₃ was further demonstrated by a reaction where both BF₃ and BPh₃ were in competition, by adding one equivalent of BF₃ and one equivalent BPh₃ simultaneously to a solution of $[(dippe)NiH]_2$ and benzonitrile in THF- d_8 . The reaction was monitored via ³¹P{¹H} NMR spectroscopy and initially showed four sets of doublets (see Supplementary Information). Two sets of doublets were located at δ = 81.8 and 65.3 ppm with ${}^{2}J_{PP}$ = 41 Hz (**2a**, 52%) and δ = 85.3 and 71.9 ppm with ${}^{2}J_{PP}$ = 20 Hz (**2b**, 18%). The other sets of doublets were located at δ = 66.3 and 59.1 ppm with ²*J*_{PP} = 56 Hz (**3a**, 15%) and δ = 84.2 and 74.6 ppm with ${}^{2}J_{PP}$ = 30.5 Hz (**3b**, 9%), with the remaining material appearing as (dippe)Ni(CN)₂. After 15 minutes at 65 °C, 3a disappeared completely and 3b (52%) was the dominant species while 2a (19%) and 2b (22%) were present in nearly equal quantities with the remainder of the material consisting of (dippe)Ni(CN)₂. After 24 hours at 65 °C, a noticeable change was observed: 2a

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(3%) was almost completely gone while **2b** (48%) was now the dominant product over 3b (28%) with the remainder being (dippe)Ni(CN)₂ (8%) and decomposition products. At this point in the reaction, one additional equivalent of BF₃ was added to see if any of the coordinated BPh₃ could be displaced, however, no changes were observed indicating that BPh₃ bonds more strongly to the nickel complexes, supporting the notion of the BF₃ reaction occurring more quickly due to the lability of BF₃ in **3a**. These results indicate that BPh₃ forms a more thermodynamically stable complex as **2b** comes to be the major species over time. **3b** appears as the kinetically preferred product as it is the dominant species early in the reaction, but is observed to decrease in favor of **2b** over time and cannot be regenerated even upon the addition of more BF₂.

The reaction with BF₃ was run at -20 °C, allowing isolation of yellow, block-like crystals of 3a suitable for X-ray structure determination (Figure 6). Table 1 shows a comparison of relevant bond distances and IR data for 1a-b, 2a**b**, and **3a**.



N1-Ni1 146.19(11), N1-C1-Ni1 71.12(9), C1-N1-B1 144.19(14).

Low-temperature NMR studies. A solution of $[(dippe)NiH]_2$ in THF- d_8 was cooled to -78 °C and treated with two equivalents of benzonitrile turning the deep red solution yellow-brown with the evolution of H₂ gas upon mixing. The sample was placed in a pre-cooled NMR probe at -60 °C and a ³¹P{¹H} NMR spectrum was collected. Two sets of doublets were observed at δ = 79.9 and 67.7 ppm with ${}^{2}J_{PP}$ = 67 Hz associated with **1a** and a new set of doublets at δ = 64.5 and 59.6 ppm with ${}^{2}J_{PP}$ = 80 Hz associated with a fluxional Ni(0)– η^2 -aryl complex **1c** (Scheme 3), as observed in previous work.¹⁷ A solution of one equivalent of BPh₃ in THF was pre-cooled to -78 °C and added to the mixture. The ³¹P{¹H] NMR spectrum showed two sets of doublets at δ = 81.8 and 65.3 ppm with ${}^{2}J_{PP}$ = 41 Hz (**2a**) and δ = 58.2 and 53.4 ppm with ${}^{2}J_{PP}$ = 80 Hz (1c). As the solution

was gradually warmed (-60 to 25 °C), 1c disappeared and only 2a remained. No evidence of BPh₃ coordinated to 1c was observed.



A second experiment was run where the BPh₃ and benzonitrile were mixed prior to the addition to the [(dippe)NiH]₂ solution at low temperature with the intention of forming **2c** with BPh₃ coordinated to the nitrogen lone pair (Scheme 4). The ³¹P{¹H} NMR spectrum showed four sets of doublets. One set of doublets was observed at δ = 64.5 and 56.7 ppm with ²*J*_{PP} = 46 Hz suspected to be the BPh₃-coordinated form of 1c (2c, 4%). A second set of doublets observed was associated with 2a (40%). The third set of doublets was associated with **2b** (40%), and the final set of doublets was observed at δ = 72.2 and 70 ppm with ²*J*_{PP} = 42 Hz (10%) and is unidentified. The remaining material represented decomposition products. As the mixture was slowly warmed to 25 °C, 2c disappeared and 2b appeared in the same amount (~4% by NMR). All of the other resonances remained unchanged. The appearance of **2b** is very important as it was never observed previously to be formed at low temperature and also did not start to appear until about four minutes at 65 °C in previous experiments. The fact that it now appears at low temperature supports the proposal that **2c** must be an important intermediate in the mechanism of Lewis acid catalyzed Ph-CN cleavage (vide infra).



Scheme 4 Reaction with benzonitrile and BPh₂ at -65 °C

Use of Lewis acids with substituted benzonitriles. A solution of [(dippe)NiH]₂ was treated with two equivalents of 4-methoxybenzonitrile or 4-methylbenzonitrile and 0.5 equivalent BPh₃ in THF-d₈ at 25 °C turning the deep red solution yellow-brown with the evolution of H₂ gas. The reactions were heated to 65 °C to produce BPh₃-coordinated C-CN cleavage adducts 5 and 6, respectively. Monitoring the F

reactions by ³¹P{¹H} NMR spectroscopy allowed a comparison with the equilibrium constants generated in previous work (Table 2).^{2b}

Table 2 Comparison of K _{eq} Data of para-Substituted Benzonitriles							
<i>p</i> -Substituted group	K _{eq} (no BPh₃)	t _{1/2} (min)	K _{eq} (w/ BPh ₃)	t _{1/2} (min)			
Н	1.62	607.5ª	large	5.99			
OCH_3	0.34	333.9	7.6 ^b	924.2			
CH ₃	0.74	464.6	17 ^b	_c			

^a Equilibrium achieved after 46 h at 54 °C.

^b Equilibrium was achieved within 48 h at 65 °C.

^c Not determined.

Previous results indicated that the presence of the parasubstituted group had an effect on the stability of the Ni(II) complex by either strengthening (withdrawing groups) or weakening (donating groups) the Ni–phenyl bond^{2b} thereby allowing a reaction to reach an equilibrium state based on the relative stabilities of the Ni(0) and Ni(II) complexes. The results of these Lewis acid experiments show that the presence of Lewis acid not only accelerates the rate of the reaction but changes the equilibrium in favor of the activated Ni(II) product. The strengthening of the Ni–CN bond by the Lewis acid appears to be more important than the effect by the para-substituents to the product stability. Therefore, Lewis acids do shift the Ph–CN cleavage equilibria to the right.

A yellow, block-like crystal of **5** and a colorless, platelike crystal of **6** suitable for X-ray diffraction were obtained and the structures were determined. Bond lengths and angles are provided in the Supporting Information.

Mechanism of Lewis acid assisted C-CN cleavage. Based on the data presented above, the following mechanism is proposed for the C-CN activation of benzonitrile by $[(dippe)NiH]_2$ in the presence of 0.5 equivalent of BPh₃ (Scheme 5). The first step of the reaction shows the dissociation of BPh₃ from **2a** to form **1a**. Evidence for this step was observed via ³¹P{¹H} NMR spectroscopy when a significant broadening of the peaks for 2a and 1a was observed when using less than one equivalent of BPh₃. When using one equivalent or greater of BPh₃, no broadening was observed as the equilibrium lies strongly in favor of 2a. Since 2a forms completely when using one equivalent or greater of BPh₃, the energy associated with BPh₃ dissociation must be added to the barrier for reactions starting from 1a. Since 2a is significantly lower in energy than **1a**, the reaction rate actually slows compared to the reaction without BPh₃.

The next step, migration of the nickel-benzonitrile complex from η^2 -nitrile **1a** to η^2 -arene **1c** was demonstrated both experimentally and via DFT calculations reported earlier by our group¹⁷ and in related calculations for the



Scheme 5 Proposed mechanism for the C–CN activation of benzonitrile by [(dippe)NiH]₂ in the presence of BPh₃

Ni(PMe₃)₂ derivative.¹⁸ This step was shown to be vital to the formation of **1b**; however, previous low-temperature NMR experiments have shown 1c to be unstable with respect to **1a**, and **1a** therefore acts to slow the reaction.^{2b,17} However, we suggest that when small quantities of BPh₃ are in solution (from BPh₃ dissociation from 2a), the Lewis acid coordinates to 1c via the lone pair of electrons on the nitrogen, forming 2c. The current low-temperature NMR studies showed the existence of 2c and its ability to disappear rapidly to form **2b** upon warming. The transient appearance of 2c, coupled with the rapid and permanent appearance of **2b**, indicates that **2c** must be significantly lower in energy than **1c** yet unstable compared to **2b**. As a result, this step, the formation of **2c** from BPh₃ and **1c**, can be considered a critical difference when less than one equivalent of BPh₃ is used. Additionally, by incorporation of BPh₃ in this step, the rate of C-CN cleavage can be accelerated by ~100-fold to account for the observed rate increase. Consequently, BPh₃ is the necessary element in this step to allow the accelerated formation of **2b** which is facilitated by conditions allowing BPh₃ dissociation from **2a**.

Another mechanism was proposed by Taw et al.^{2e} showing that the Lewis acid coordinates directly to the metal center before migrating to the nitrogen of the aryl nitrile. The order of addition experiment described earlier shows no evidence of the Ni–BPh₃ complex under specific reaction conditions indicating that this mechanism is inappropriate for this system.

In summary, reactions of $[(dippe)NiH]_2$ with benzonitrile and varying concentrations of Lewis acids (primarily BPh₃ and BF₃) have shown a dramatic variation of reaction rate compared to the same reaction without Lewis acids. When less than one equivalent of Lewis acid is used, the reaction rate is as much as 100 times greater. Boron exchange was observed with less than one equivalent of Lewis acid

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allowing the formation of a Ni(0)– η^2 -aryl complex (observed by low-temperature NMR and calculations) to which the Lewis acid is postulated to re-coordinate as the rate-limiting step allowing the formation of a stable Ni(II) product. When one equivalent or greater of Lewis acid is used, the reaction shows dramatic inhibition even compared to the reaction without Lewis acid. Lewis acid dissociation can be considered a rate-limiting step under these conditions. Other Lewis acids (BEt₃, AlF₃, SnF₄, or SnPh₄) proved ineffective (see Supporting Information).

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1590801.

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- (14) **Preparation of (dippe)Ni(h²-PhCNBPh₃), 2a.** A solution of $[(dippe)NiH]_2$ (0.01 g, 0.016 mmol) in THF-*d*₈ was combined with benzonitrile (3.3 μL, 0.032 mmol) producing a yellow-brown solution with the evolution of H₂ gas. BPh₃ (0.0072 g, 0.032 mmol) was added and the solution was transferred to an NMR tube. The reaction was observed via NMR spectroscopy and the solution was collected in a vial and allowed to slowly crystallize at room temperature giving orange, block-like crystals (80% yield by NMR). ¹H NMR (THF-*d*₈): δ = 0.75–1.2 (m, 24 H, ⁱPr-CH₃), 1.5–1.7 (m, 4 H, PCH₂CH₂P), 1.9–2.1 (m, 4H, ⁱPr-CH), 6.85–7.7 shows overlapping multiplets in the aryl region. ³¹P{¹H} NMR: δ = 81.8 (d, ²J_{PP} = 41 Hz), 65.3 (d, ²J_{PP} = 41 Hz). IR v(CN) = 1755 cm⁻¹.

Preparation of (dippe)Ni(CNBPh₃)(Ph), 2b. A solution of [(dippe)NiH]₂ (0.01 g, 0.016 mmol) in THF-*d*₈ was combined with benzonitrile (3.3 μL, 0.032 mmol) producing a yellow-brown solution with the evolution of H₂ gas. BPh₃ (0.0072 g, 0.032 mmol) was added and the solution was transferred to an NMR tube. The reaction was heated to 65 °C and observed via NMR spectroscopy for 6 days. The solution was collected in a vial and allowed to slowly crystallize at room temperature giving orange, needle-like crystals (88% yield by NMR). ¹H NMR (THF-*d*₈): δ = 0.75–1.2 (m, 24 H, ⁱPr-CH₃), 1.5–1.7 (m, 4 H, PCH₂CH₂P), 2.2–2.3 (m, 4H, ⁱPr-CH), 7.5–7.7 shows overlapping multiplets in the aryl region. ³¹P{¹H} NMR: δ = 85.3 (d, ²J_{PP} = 20 Hz), 73.9 (d, ²J_{PP} = 20 Hz). IR v(CN) = 2170 cm⁻¹.

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