

## Development of a Palladium on Boron Nitride Catalyst and its Application to the Semihydrogenation of Alkynes

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**Abstract:** The simple preparative method for a novel palladium supported on boron nitride catalyst (Pd/BN) was accomplished. Pd/BN is widely applicable for the semihydrogenation of mono- as well as disubstituted alkynes to furnish the corresponding alkenes in the presence of diethylenetriamine (DETA), which exhibits both an unprecedented acceleration effect toward the semihydrogenation and a suppression effect with regard to the overhydrogenation to alkanes.

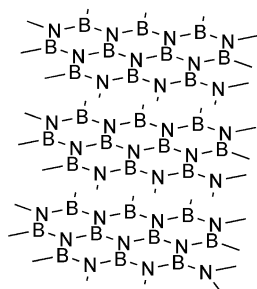
**Keywords:** alkynes; boron nitride; diethylenetriamine (DETA); heterogeneous catalysis; Pd/BN catalyst; semihydrogenation

The semihydrogenation of alkynes<sup>[1]</sup> is a useful synthetic method for alkenes and only a few methods using homogeneous<sup>[2–8]</sup> and heterogeneous<sup>[9–28]</sup> catalysts have been reported in the literature. However, an elaborate experimental set-up and strict monitoring of the reaction process are still required to prevent overreduction to alkanes. Especially, the semihydrogenation of monosubstituted alkynes to the corresponding monosubstituted alkenes<sup>[3,19–22]</sup> is an extremely difficult and challenging reaction in connection with the significant synthesis of the synthons of the functional polymers, total syntheses and so on.<sup>[15,23–27]</sup> Meanwhile, heterogeneous Pd catalysts are practical and appropriate in terms of green chemistry due to their stability under atmospheric conditions, easily separable property without Pd leaching, reusability and so on. Although Lindlar's catalyst [Pd/CaCO<sub>3</sub> poisoned by Pb(OAc)<sub>2</sub> and quinoline]<sup>[9]</sup> is most frequently utilized as a heterogeneous semihydrogenation catalyst, it possesses some disadvantages such as the use of toxic Pb(OAc)<sub>2</sub> during the catalyst preparation and it cannot be used for the semihydro-

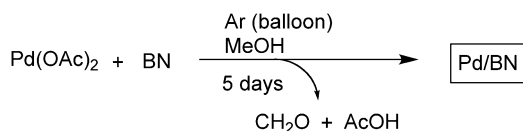
genation of monosubstituted alkynes. We now report an efficient semihydrogenation method for mono- as well as disubstituted alkynes using an easily prepared and environmental friendly novel heterogeneous Pd catalyst.

We have recently developed useful heterogeneous catalysts {e.g., Pd/C-ethylenediamine complex [Pd/C(en)],<sup>[29]</sup> Pd-polyethyleneimine complex (Pd/PEI),<sup>[30]</sup> Pd/C-diphenyl sulfide complex [Pd/C(Ph<sub>2</sub>S)],<sup>[31]</sup> Pd-fibroin complex [Pd/Fib]<sup>[32]</sup> and Pd-molecular sieves complex (Pd/MS3 Å)<sup>[33]</sup>} possessing specific characteristics and suppressed catalytic activities to enable the chemoselective hydrogenation among various reducible functionalities such as N-Cbz, benzyl ether, aromatic ketone, nitro, alkyne, alkene, azido and so on. Our suppression methodologies for the Pd catalyst's activity are classified into two categories: (i) suppression by the coordination-induced catalyst poisoning effect using the lone pairs of amines or sulfides,<sup>[34]</sup> such as Pd/C(en), Pd/PEI<sup>[35]</sup> and Pd/C(Ph<sub>2</sub>S), (ii) suppression due to the catalyst supports utilizing their characteristic properties as a material, such as Pd/Fib and Pd/MS3 Å.

We have focused on boron nitride (BN) as a catalyst support. BN is a benign powder possessing a hexagonally-shaped crystal structure composed of continuous boron-nitrogen bonds (Figure 1), and the numerous lone pairs on the nitrogen atoms were expected to coordinate with the Pd metal and suppress the catalyst activity for hydrogenation. Pd on BN (Pd/BN) could be easily prepared by just stirring the colorless BN in a rust-colored MeOH solution of Pd(OAc)<sub>2</sub> [0.5 wt% of Pd metal vs. BN was used as Pd(OAc)<sub>2</sub>, Scheme 1].<sup>[32,33]</sup> After stirring at room temperature for 5 days, reduced Pd(0) was supported on BN to give 0.3 wt% Pd/BN<sup>[36,37]</sup> as a grey powder. STEM analysis showed that the Pd metal was agglutinated to form ca. 10 nm size particles with a high dispersivity on BN regardless of the quite small specific surface area of



**Figure 1.** Structure of boron nitride (BN).

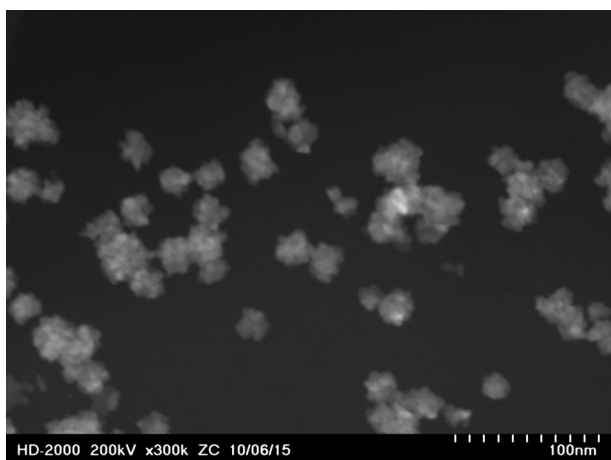


**Scheme 1.** Preparation of our Pd/BN catalyst.

BN ( $5 \text{ m}^2 \text{ g}^{-1}$ , the general specific surface area of Pd/C is *ca.*  $850 \text{ m}^2 \text{ g}^{-1}$ , Figure 2).

Pd/BN possesses a reasonably lower catalyst activity due to a cluster formation of the Pd metal. Alkyne and alkene functionalities could be selectively hydrogenated in MeOH under an  $\text{H}_2$  atmosphere at  $25^\circ\text{C}$  in the presence of ketone, aryl halide, nitro, N-Cbz, benzyl ester and benzyl ether functionalities (Table 1). Meanwhile, the reduction control (semihydrogenation) between the alkyne and alkene functionalities could not be accomplished by the independent application of Pd/BN (Table 1, entries 1–3; Table 2, entry 1).

Amines are generally known to suppress the catalyst activity of supported platinum group metal catalysts due to the metal coordination effect. Therefore, ethylenediamine constructing a rigid five-membered cyclic coordination complex with metals was utilized as an efficient additive to control the semihydrogenation



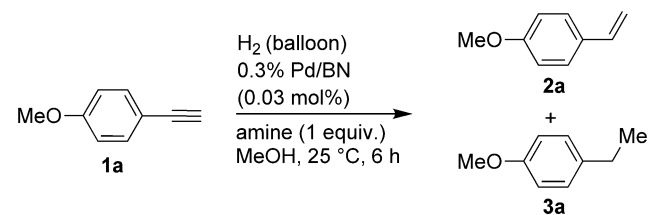
**Figure 2.** STEM of 0.3% Pd/BN catalyst.

**Table 1.** Pd/BN catalyzed the chemoselective hydrogenation in MeOH.

Entry	Substrate	Product	Time [h]	Yield [%]
1		–	6	N.R. <sup>[a]</sup>
2		–	6	N.R. <sup>[a]</sup>
3			6	100
4			6	97
5			3	99

<sup>[a]</sup> N.R. = no reaction.

**Table 2.** Effect of amines on the semihydrogenation.



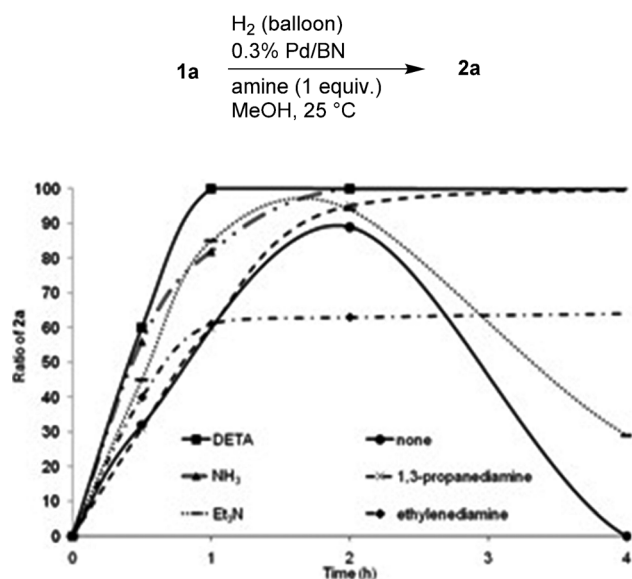
Entry	Amine	Ratio <sup>[a]</sup> <b>1a:2a:3a</b>
1 <sup>[b]</sup>	None	0:0:100
2		35:65:0
3	$\text{Et}_3\text{N}$	0:0:100
4	$\text{NH}_3$	0:100:0
5		0:100:0
6		0:100 (99) <sup>[c]</sup> :0

<sup>[a]</sup> The ratio was determined by  $^1\text{H}$  NMR and GC/MS.

<sup>[b]</sup> Ratio of **1a:2a:3a** was 68:32:0 (at 30 min), 35:65:trace (at 1 h) and 0:89:11 (at 2 h).

<sup>[c]</sup> Isolated yield [%].

tion of alkynes in the literature.<sup>[10j,k,17b]</sup> On the other hand, we recently found that  $\text{Et}_3\text{N}$  possessing a relatively weak coordination property to platinum metals accelerated the Pd/C-catalyzed hydrogenation of alkenes<sup>[38]</sup> and chloroarenes.<sup>[39]</sup> We particularly investigated the addition effect of amines to achieve the



**Figure 3.** Time-course study of the semihydrogenation in the presence of amines.

moderate depression toward the Pd/BN-catalyzed semihydrogenation of alkynes by comparison of the products ratio after the 6 h reaction (Table 2) and the time-course study based on the generated alkene ratio (Figure 3) using 4-methoxyethynylbenzene (**1a**) as a substrate.

Although the reaction with ethylenediamine could afford only alkenes without overreduction to the alkane (**3a**), 35% of the substrate (**1a**) still remained unchanged after a 6 h reaction [Table 2, entry 2; Figure 3 (◆)]. While Et<sub>3</sub>N was found to rather accelerate the semihydrogenation to form **2a**, the overreduction of **2a** to **3a** also smoothly proceeded and only **3a** was obtained after 6 h [Table 2, entry 3; Figure 3 (–)]. NH<sub>3</sub> [Table 2, entry 4; Figure 3 (▲)], 1,3-propanediamine [Table 2, entry 5; Figure 3 (×)] and diethylenetriamine (DETA) [Table 2, entry 6; Figure 3 (■)] successfully suppressed the overreduction to produce **2a** as the sole product, and NH<sub>3</sub> and DETA effectively accelerated the semihydrogenation to the alkene (**2a**) and completely suppressed the overreduction to the alkane (**3a**). DETA was chosen as the most efficient additive because the Pd/BN-catalyzed semihydrogenation was more smoothly completed within 1 h (see Figure 3) and no overhydrogenated product (**3a**) was produced even after 6 h reaction.<sup>[40]</sup>

The Pd/BN-DETA combination is widely applicable for the selective semihydrogenation of various monosubstituted alkynes (Table 3). Not only arylalkynes (entries 1–5) but also aliphatic alkynes (entries 6–13) could also be transformed into the corresponding alkenes in nearly quantitative isolated yields with quite high selectivities. It is noteworthy that the present reaction was adaptable to the semihydrogenation of substrates bearing unprotected amine (entry 3)

**Table 3.** Scope and limitation of semihydrogenation of alkynes in the presence of DETA.

$\text{H}_2$  (balloon)  
 0.3% Pd/BN  
 (0.03 mol%)  
 DETA (X equiv.)  
 MeOH, 25 °C, 6 h

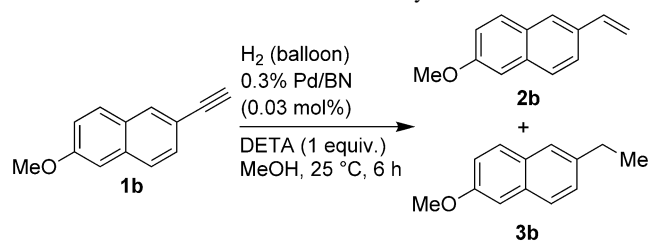
$\text{R}^1\text{C}\equiv\text{CR}^2 \xrightarrow{\hspace{10em}} \text{R}^1\text{C}=\text{CR}^2 + \text{R}^1\text{CH}_2\text{CR}^2$

Entry	Product	Ratio 1:2:3	X	Yield [%]
1		0:95:5	1.0	–
2		0:100:0	1.0	99
3		0:98:2	2.0	90
4		0:100:0	1.3	96
5		5:95:0	1.0	95
6		0:98:2	1.2	97
7		0:99:1	1.1	96
8		0:100:0	1.0	96
9		0:95:5	1.5	95
10		0:100:0	0.5	97 <sup>[a]</sup>
11		0:99:1	0.1	90 <sup>[b]</sup>
12		0:98:2	1.5	88
13		0:100:0	0.8	99
14		0:100:0	1.0	98
15		2:92:6	1.0	92
16		4:94:2	1.0	90 <sup>[a]</sup>

<sup>[a]</sup> At 50 °C.

<sup>[b]</sup> THF was used instead of MeOH to prevent the ester exchange.

and hydroxy groups (entries 9 and 13); also TBS ether (entries 7 and 10), benzyl ether (entry 8), N-Cbz (entry 4) and nitro (entry 5) groups were tolerated under the hydrogenation conditions. Various disubstituted alkynes were also semihydrogenated to the corresponding *cis*-alkenes in high yields and selectivities

**Table 4.** Reuse test of the Pd/BN catalyst.

Run	Ratio <b>1b</b> : <b>2b</b> : <b>3b</b>	Yield [%] <sup>[a]</sup>
1 <sup>st</sup>	0:100:0	99
2 <sup>nd</sup>	0:100:0	98
3 <sup>rd</sup>	0:100:0	99

<sup>[a]</sup> Isolated yield.

(entries 14–16). The formation of the corresponding *trans*-isomer was never observed under these reaction conditions.

Pd/BN could be easily recovered merely by simple filtration and rinsing with MeOH and water. The recovered Pd/BN catalyst was found to retain its catalyst activity and could be reused for at least three times (Table 4).<sup>[41]</sup>

In summary, we have developed a simple preparative method for Pd/BN, a chemoselective hydrogenation catalyst. Pd/BN is widely applicable for the selective semihydrogenation of mono- as well as disubstituted alkynes to the corresponding alkenes in the presence of DETA. Furthermore, we have shown that DETA exhibits both an unprecedented acceleration effect during the semihydrogenation of alkynes to alkenes and a suppression effect with regard to the overhydrogenation to alkanes. The present environmentally friendly method is useful in laboratory and industry scale reactions. The simplicity of this method and the reusability of Pd/BN make them attractive new tools for organic and process chemists.

## Experimental Section

### Preparation of Pd/BN Catalyst

To a solution of Pd(OAc)<sub>2</sub> (28.1 mg, including 13.3 mg of Pd metal; 0.5 wt% Pd metal vs. BN) in MeOH (50 mL) was added boron nitride (BN) (2.66 g), and the suspension was stirred at room temperature for 5 days. The resulting suspension was filtered and the obtained solid was washed with MeOH and H<sub>2</sub>O, then dried under reduced pressure to give the 0.3% Pd/BN catalyst as a grey powder; yield: 2.6 g.

### Typical Procedure for the Chemoselective Hydrogenation (Table 1)

A mixture of a substrate (0.25 mmol), 0.3% Pd/BN (0.03 mol% of the substrate, 2.7 mg) in MeOH (1 mL) was

stirred under an ordinary (balloon) hydrogen pressure at 25 °C. The resulting mixture was diluted with Et<sub>2</sub>O and filtered through a membrane filter (Millipore, Millex®-LH, 0.45 μm). The filtrate was concentrated under reduced pressure to provide the product.

### Typical Procedure for the Semihydrogenation of Alkynes

A mixture of a substrate (0.25 mmol), 0.3% Pd/BN (0.03 mol% of the substrate, 2.7 mg) and DETA (0.25 mmol, 27 μL) in MeOH (1 mL) was stirred under an ordinary (balloon) hydrogen pressure at 25 °C for 6 h. The resulting mixture was diluted with Et<sub>2</sub>O or hexanes (10 mL) and H<sub>2</sub>O (10 mL), then filtered through a membrane filter (Millipore, Millex®-LH, 0.45 μm). The filtrate was separated into two layers and the aqueous layer was further extracted with Et<sub>2</sub>O or hexanes (10 mL × 2). The combined organic layers were dried over MgSO<sub>4</sub>, and concentrated under vacuum to give the product. If purification was required, the product was isolated after flash column chromatography.

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## References

- [1] a) S. Nishimura, in: *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*, Wiley-Interscience, New York, **2001**; b) A. M. Kluwer, C. J. Elsevier, in: *The Handbook of Homogeneous Hydrogenation*, Vol. 1, (Eds: J. G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, **2007**, pp 375–411.
- [2] a) M. W. van Laren, C. J. Elsevier, *Angew. Chem.* **1999**, *111*, 3926–3929; *Angew. Chem. Int. Ed.* **1999**, *38*, 3715–3717; b) M. W. van Laren, M. A. Duin, C. Klerk, M. Naglia, D. Rogolino, P. Pelagatti, A. Bacchhi, C. Pelizzi, C. J. Elsevier, *Organometallics* **2002**, *21*, 1546–1553; c) A. Dedieu, S. Humbel, C. J. Elsevier, C. Grauffel, *Theor. Chem. Acc.* **2004**, *112*, 305–312; d) J. W. Sprengers, J. Wassenaar, N. D. Clement, K. J. Cavell, C. J. Elsevier, *Angew. Chem.* **2005**, *117*, 2062–2065; *Angew. Chem. Int. Ed.* **2005**, *44*, 2026–2029; e) P. Hauwert, G. Maestri, J. W. Sprengers, M. Catellani, C. J. Elsevier, *Angew. Chem.* **2008**, *120*, 3267–3270; *Angew. Chem. Int. Ed.* **2008**, *47*, 3223–3226; f) S. Warsink, R. M. Drost, M. Lutz, A. L. Spek, C. J. Elsevier, *Organometallics* **2010**, *29*, 3109–3116; g) S. Warsink, I. H. Chang, J. J. Weigand, P. Hauwert, J. T. Chen, C. J. Elsevier, *Organometallics* **2010**, *29*, 4555–4561; h) P. Hauwert, R. Boerleider, S. Warsink, J. J. Weigand, C. J. Elsevier, *J. Am. Chem. Soc.* **2010**, *132*, 16900–16910.
- [3] H. S. La Pierre, J. Arnold, F. D. Toste, *Angew. Chem.* **2011**, *123*, 3986–3989; *Angew. Chem. Int. Ed.* **2011**, *50*, 3900–3903.
- [4] R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* **1976**, *98*, 2143–2147.



- [5] P. Pelagatti, A. Leporati, M. Carcelli, M. Costa, A. Bacchi, G. Pelizzi, C. Pelizzi, *J. Chem. Soc. Dalton Trans.* **1998**, 2715–2721.
- [6] M. Sodeoka, M. Shibasaki, *J. Org. Chem.* **1985**, *50*, 1147–1149.
- [7] E. W. Stern, P. K. Maples, *J. Catal.* **1972**, *27*, 120–133.
- [8] J. Liu, R. Hua, T. Liu *J. Org. Chem.* **2010**, *75*, 2966–2970.
- [9] H. Lindlar, R. Dubuis, *Org. Synth. Coll. Vol. 5*, **1973**, 880–883.
- [10] a) K. N. Campbell, L. T. Eby, *J. Am. Chem. Soc.* **1941**, *63*, 216–218; b) K. Ahmad, F. M. Strong, *J. Am. Chem. Soc.* **1948**, *70*, 1699–1700; c) R. A. Max, F. E. Deatherage, *J. Am. Oil Chem. Soc.* **1951**, *28*, 110–114; d) S. A. Fusari, K. W. Greenlee, J. B. Brown, *J. Am. Oil Chem. Soc.* **1951**, *28*, 416–420; e) D. R. Howon, R. H. Davis, *J. Org. Chem.* **1951**, *16*, 1405–1413; f) W. F. Huber, *J. Am. Chem. Soc.* **1951**, *73*, 2730–2733; g) W. Oroshnik, G. Karmas, A. D. Mevane, *J. Am. Chem. Soc.* **1952**, *74*, 295–304; h) N. A. Khan, *J. Am. Chem. Soc.* **1952**, *74*, 3018–3022; i) J. A. Knight, J. H. Diamond, *J. Org. Chem.* **1959**, *24*, 400–403; j) C. A. Brown, V. K. Ahuja, *J. Chem. Soc. Chem. Commun.* **1973**, 553–554; k) C. A. Brown, V. K. Ahuja, *J. Org. Chem.* **1973**, *38*, 2226–2228.
- [11] a) W. Oroshnik, G. Karmas, A. D. Mebane, *J. Am. Chem. Soc.* **1952**, *74*, 3807–3813; b) W. Oroshnik, A. D. Mebane, *J. Am. Chem. Soc.* **1954**, *76*, 5719–5736; c) C. A. Brown, V. K. Ahuja, *J. Chem. Soc. Chem. Commun.* **1973**, 553–554.
- [12] Y. Nitta, T. Imanaka, S. Teranishi, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3579–3580.
- [13] a) J. J. Brunet, P. Gallois, P. Caubere, *J. Org. Chem.* **1980**, *45*, 1937–1945; b) P. Gallois, J. J. Brunet, P. Caubere, *J. Org. Chem.* **1980**, *49*, 1946–1950.
- [14] J. J. Brunet, P. Caubere, *J. Org. Chem.* **1984**, *49*, 4058–4060.
- [15] N. M. Yoon, K. B. Park, H. J. Lee, J. Choi, *Tetrahedron Lett.* **1996**, *37*, 8527–8528.
- [16] a) M. Armbrüster, K. Kovnir, M. Behrens, D. Teschner, Y. Grin, R. Schlögl, *J. Am. Chem. Soc.* **2010**, *132*, 14745–14747; b) A. Ota, M. Armbrüster, M. Behrens, D. Rosenthal, M. Friedrich, I. Kasatkin, F. Girgsdies, W. Zhang, R. Wagner, R. Schlögl, *J. Phys. Chem. C* **2011**, *115*, 1368–1374.
- [17] a) M. Gruttadauria, R. Noto, G. Deganello, L. F. Liotta, *Tetrahedron Lett.* **1999**, *40*, 2857–2858; M. Gruttadauria, L. F. Liotta, R. Noto, G. Deganello, *Tetrahedron Lett.* **2001**, *42*, 2015–2017.
- [18] Á. Mastalir, Z. Király, G. Szöllösi, M. Bartók, *J. Catal.* **2000**, *194*, 146–152.
- [19] R. Nishino, M. Sugiura, S. Kobayashi, *Org. Biomol. Chem.* **2006**, *4*, 992–995.
- [20] a) F. Alonso, I. Osante, M. Yus, *Adv. Synth. Catal.* **2006**, *348*, 305–308; b) F. Alonso, I. Osante, M. Yus, *Tetrahedron* **2007**, *63*, 93–102.
- [21] Z. Shao, C. Li, X. Chen, M. Pang, X. Wang, C. Liang, *ChemCatChem* **2010**, *2*, 1555–1558.
- [22] M. W. Tew, H. Emerich, J. A. van Bokhoven, *J. Phys. Chem. C* **2011**, *115*, 8457–8465.
- [23] Á. Mastalir, Z. Király, *J. Catal.* **2003**, *220*, 372–381.
- [24] J. Panpranot, K. Phandinthong, T. Sirikajorn, M. Arai, P. Praserttham, *J. Mol. Catal. A* **2007**, *261*, 29–35.
- [25] S. D. Dominguez, Á. B. Murcia, B. K. Pradhan, Á. L. Solano, D. C. Amorós, *J. Phys. Chem. C* **2008**, *112*, 3827–3834.
- [26] P. Weerachawanasak, O. Mekasuwandumrong, M. Arai, S. Fujita, P. Praserttham, J. Panpranot, *J. Catal.* **2009**, *262*, 199–205.
- [27] Y. Zhao, Q. Liu, J. Li, Z. Liu, B. Zhou, *Synlett* **2010**, 1870–1872.
- [28] J. Hori, K. Murata, T. Sugai, H. Shinohara, R. Noyori, K. Arai, N. Kurono, T. Ohkuma, *Adv. Synth. Catal.* **2009**, *351*, 3143–3149.
- [29] K. Hattori, H. Sajiki, K. Hirota, *Tetrahedron* **2001**, *57*, 2109–2114.
- [30] a) H. Sajiki, S. Mori, T. Ohkubo, T. Ikawa, A. Kume, T. Maegawa, Y. Monguchi, *Chem. Eur. J.* **2008**, *14*, 5109–5111; b) S. Mori, T. Ohkubo, T. Ikawa, A. Kume, T. Maegawa, Y. Monguchi, H. Sajiki, *J. Mol. Catal. A: Chem.* **2009**, *307*, 77–87.
- [31] A. Mori, T. Mizusaki, M. Kawase, T. Maegawa, Y. Monguchi, S. Takao, Y. Takagi, H. Sajiki, *Adv. Synth. Catal.* **2008**, *350*, 406–410.
- [32] T. Ikawa, H. Sajiki, K. Hirota, *Tetrahedron* **2005**, *61*, 2217–2231.
- [33] T. Maegawa, T. Takahashi, M. Yoshimura, H. Suzuka, Y. Monguchi, H. Sajiki, *Adv. Synth. Catal.* **2009**, *351*, 2091–2095.
- [34] Amino-poisoned chemoselective hydrogenation: a) H. Sajiki, K. Hirota, *Tetrahedron* **1998**, *54*, 13981–13996; sulfur-poisoned chemoselective hydrogenation: b) A. Mori, T. Mizusaki, Y. Monguchi, H. Sajiki, *Org. Lett.* **2006**, *8*, 3279–3281.
- [35] Although the Pd/C-polyethyleneimine complex (Pd/PEI) enabled the semihydrogenation of both the mono- and disubstituted alkynes, careful reaction conditions such as the solvent for each substrate, were required. Furthermore, the selectivities to form alkenes were not optimized and the reuse of the catalyst was not applicable.
- [36] Pd/BN prepared from Pd(acac)<sub>2</sub> and anhydrous hydrazine in aprotic solvents was used for the oxidation of CH<sub>3</sub>: G. Postole, A. Gervasini, A. Auroux, B. Bonnetot, *Mater. Sci. Forum* **2006**, *518*, 203–210.
- [37] Pd metal absorbed on the BN was nearly 0.3 wt% of the catalyst based on an ICP analysis.
- [38] H. Sajiki, K. Hirota, *Tetrahedron* **1998**, *54*, 13981–13996.
- [39] Y. Monguchi, A. Kume, K. Hattori, T. Maegawa, H. Sajiki, *Tetrahedron* **2006**, *62*, 7926–7933.
- [40] The use of 0.03 mol% of 1% Pd/C instead of Pd/BN could not achieve the selective synthesis of the alkene (**2a**) in the presence of DETA.
- [41] The catalytic activity of the reused Pd/BN was slightly reduced due to the small amount of Pd leaching (2.2%) after the first semihydrogenation. The results of Pd metal leaching, and the time course study using reused Pd/BN are described in the Supporting Information.