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Remarkable Catalytic Property of Nanoporous Gold on Activation of Diborons for Direct Diboration of Alkynes

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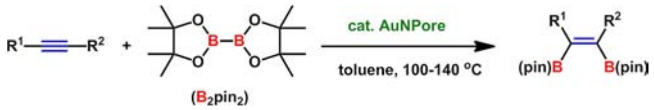
ABSTRACT



A novel catalytic property of nanoporous gold for activation of bis(pinacolato)diboron has been reported that allows the direct diboration of alkynes to proceed sufficiently in a heterogeneous process. The experimental results revealed that the nanoporous gold catalyst is able to cleave the B—B bond of bis(pinacolato)diboron without using any additives.

In the past decade, efforts to develop new catalytic properties of nanoporous gold (AuNPore) demonstrated that AuNPore is a promising, green, and robust heterogeneous catalyst candidate for diverse molecular transformations.[1−4] The AuNPore catalyst dealloyed from the Au—Ag alloy[5] has randomly oriented ligaments with a hyperboloid-like shape and nanopore channels and possesses a high density of surface steps and kinks that are active for chemical reactions.[6] The AuNPore has high surface area, high stability for versatile chemicals, high reusability, and no toxic nature, and it is recovered readily from the reaction mixture. Moreover, unlike the gold nanoparticle catalysts,[7] the AuNPore possesses high thermal stability against coarsening, and it exhibits catalytic activity without oxide supports which is helpful for understanding the insight of the reaction mechanism and catalytic origins.[6] The AuNPore catalyst has been successfully

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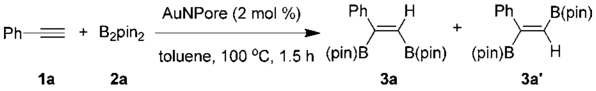
applied to the various oxidation reactions, for example, gas-phase oxidation of CO or MeOH, and liquid-phase oxidation of alcohol or organosilane has been reported to show remarkable selectivities and efficiencies.[1−3] Recently, we demonstrated that AuNPore can be used as a robust catalyst for the selective hydrogenation of alkynes or quinolines using organosilane as a reducing reagent.[4] However, so far, the catalytic applications of AuNPore are mainly limited to selective oxidation and reduction reactions. Herein, we report a novel catalytic property of AuNPore on activation of a B−B bond of bis(pinacolato)diboron (B_2pin_2) in direct diboration of alkynes without using any additives, affording the corresponding 1,2-diborylalkenes in good to high yields with high *cis*-selectivities. To the best of our knowledge, this is the first demonstration that gold can cleave a B−B bond directly without using any additives.

Catalytic direct diboration of alkynes with diborons is a powerful synthetic method for construction of the diboryl alkenes which are key intermediates for concise synthesis of useful complex molecules by functionalization of both C−B bonds.[8] Since the first discovery of the Pt-catalyzed diboration of alkynes by Suzuki, Miyaura and co-workers in 1993,[9a] various homogeneous transition metal-catalyzed diborations have been reported.[8,9] However, taking into consideration the chemical and pharmaceutical process, the major drawbacks of homogeneous catalysis, such as *metal contamination* into products and inability to recover the catalyst for reuse, limit its application in industrial interest, biomolecules, and materials science. To date, only two examples of heterogeneous diboration of alkynes have been reported.[10] For example, Braunschweig et al. reported the Pt sponge- or Pd/C-catalyzed diboration of propyne and 2-butyne using metal-based [2]borametalloarenophanes as a special diboron source.[10a] Corma et al. reported the diboration of alkynes using the platinum nanoparticles (PtNPs) supported on magnesia as catalyst at high temperature (160 °C), in which the reaction was proposed to proceed through a homogeneous process.[10b]

The AuNPore catalyst was prepared by dealloying of a monolithic $Au_{30}Ag_{70}$ alloy in 70% nitric acid as an electrolyte at rt for 18 h.[4a] The dealloyed thin film AuNPore possesses a bicontinuous porous structure with an average diameter of ∼30 nm for both ligaments and nanopores, whose scanning electronic microscopy (SEM) and transmission electron microscopy (TEM) images have been illustrated in the previous reports (Figure S1, Supporting Information).[4a] The cylindrical shape of ligament from high resolution TEM image reveals a very high density of atomic steps and kinks at curved surface, suggesting the presence of a high concentration of low-coordination surface atoms.[4,6]

Table 1. Screening of Nanoporous Metal Catalysts for Diboration of Phenylacetylene (**1a**)[a]



entry	catalyst	yield of **3a** and **3a′**[b] (%)
1	PtNPore[c]	99 (100:0)[d]
2	AuNPore	96 (93)[e] (97:3)[d] (97, 97)[f]
3	AuCl	0
4	Au−Ag alloy	0
5	PdNPore	0
6[c]	CuNPore	0
7[d]	AgNPore	0

[a] Reaction conditions: **1a** (1 mmol), **2a** (1.5 mmol), toluene (2 mL), and catalyst (2 mol %) at 100 °C for 1.5 h. [b] ^{1}H NMR yield determined using CH_2Br_2 as an internal standard. [c] PtNPore (10 mol %) was used for 40 h. [d] The ratio of **3a** and **3a′**. [e] Isolated yield. [f] The yields of the second and third uses of the catalyst. AuNPore (5 mol %) was used.

Initially, the distinct catalytic property of both homogeneous Pt(0) catalysts and PtNPs on diboration of alkynes led us to investigate the catalytic activity of the nanoporous platinum (PtNPore) in the reaction of phenylacetylene (**1a**) (1 mmol) with B_2pin_2 (**2a**) (1.5 mmol) in toluene at 100 °C (Table 1). The PtNPore catalyst prepared from Pt−Cu alloy[11] afforded the corresponding 1,2-diborylalkene (**3a**) as a sole *cis*-adduct in 99% yield within 40 h (entry 1). However, the leaching experiments and inductively coupled plasma (ICP-MS) showed that Pt atoms in PtNPore catalyst were leached to the reaction solution. For example, after heating the reaction of **1a** and **2a** for 11 h in the presence of PtNPore catalyst in toluene, a part of the supernatant was transferred to the other reaction vessel and the yield of **3a** was 54%. After continuous heating for 35 h, the yield of **3a** from the supernatant in the absence of catalyst was increased to 99%, while the residue containing PtNPore catalyst also produced **3a** in 99% yield (Scheme S1, Supporting Information). The ICP-MS analysis of the reaction in entry 1 showed that 280 ppm of Pt was leached after reaction. These results clearly indicated the reaction proceeds through a homogeneous process catalyzed by the leached Pt species in solution. To our delight, the AuNPore catalyst exhibited a remarkably increased activity for the present diboration; the reaction was completed within 1.5 h, giving the corresponding *cis*-adduct **3a** in a high yield along with a small amount of *trans*-adduct **3a′** (entry 2). The leaching experiments and ICP-MS analysis indicated that no gold catalyst was leached at all to the solution during the reaction and no other metals such as Pt

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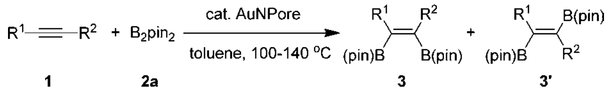
and Pd atoms were detected at ppb levels by ICP-MS, suggesting that the reaction was catalyzed by the AuNPore catalyst and not by the adventitious Pt or Pd catalyst which sometimes comes from the used glassware or chemicals (Scheme S2, Supporting Information). Moreover, the reactions with homogeneous catalysts such as AuCl and the AuNPore precursor, Au–Ag alloy, are totally inactive (entries 3 and 4). Other nanoporous metal catalysts such as nanoporous palladium (PdNPore) prepared from Pd–Al alloy,[12] nanoporous copper (CuNPore) prepared from Cu–Mn alloy,[13] and nanoporous silver (AgNPore) prepared from Ag–Al alloy[4b,14] were totally inactive for the present diboration (entries 5–7). Surprisingly, among various solvents tested, only toluene afforded the corresponding 1,2-diborylalkene in high yield, and other solvents such as DMF (trace), CH_3CN (trace), THF (trace), 1,4-dioxane (6%), and octane (0%) were almost ineffective. The AuNPore catalyst was easily removed by taking out the skeleton catalyst from the reaction mixture. The recovered AuNPore catalyst exhibited high recyclability without decreasing the catalytic activity after reusing for two more cycles (entry 2). The nanoporous structure of AuNPore did not show the obvious changes after the third run compared to that of the fresh AuNPore from the SEM images (Figure S1, Supporting Information). Other diborons instead of B_2pin_2 in the presence of AuNPore in toluene were examined as shown in Scheme S3 (Supporting Information). For example, bis(hexylene glycolato)diboron (B_2hex_2) (**2b**), which has good solubility in toluene, was still active, giving the corresponding product **3bb** (Scheme S4, Supporting Information) in 32% yield with a 93:7 mixture of *cis*- and *trans*-adducts, whereas the use of bis(neopentyl glycolato)diboron (B_2neop_2) (**2c**) and bis(catecholato)diboron (B_2cat_2) (**2d**) did not produce the corresponding 1,2-diborylalkenes.

The catalytic activity of the AuNPore was further examined with various terminal and internal alkynes using B_2pin_2 as a diboron source in toluene as shown in Table 2. Both aryl and aliphatic terminal alkynes were well tolerated, while in each case a small amount of *trans*-adducts was observed. The diboration of aryl terminal alkynes bearing an electron-donating group such as methyl or methoxy group on the benzene ring proceeded smoothly to afford the corresponding 1,2-diboryl alkenes **3** and **3′** in high yields (entries 1–4). The sterically hindered *ortho*-substituted aryl alkynes **1c** and **1e** showed higher *cis*-selectivities compared to the sterically less-hindered *para*-substituted aryl alkynes **1b** and **1d** (entries 1 and 3 vs 2 and 4). The terminal arylalkyne with an electron-withdrawing group at the *para*-position of the benzene ring (**1f**) also underwent diboration efficiently with higher *cis*-selectivity than that of the electron-rich alkynes **1b** and **1d** (entry 5). The terminal aliphatic alkynes (**1g**–**i**) were also active, producing the corresponding diboration products in good to high yields with high *cis*-selectivities (entries 6–8). In contrast to the terminal alkynes, the diborations with internal alkynes exhibited an exclusive *cis*-selectivity under the standard conditions. 1,2-Diphenylethyne (**1j**) is a suitable substrate for the present diboration, producing the corresponding product **3j** in 99% yield without its *trans*-adduct (entry 9). The reactions with the alkyl-substituted internal alkynes such as prop-1-yn-1-ylbenzene (**1k**), dec-2-yne (**1l**), oct-4-yne (**1m**), and 1,4-dimethoxybut-2-yne (**1n**) also gave satisfactory chemical yields of the corresponding 1,2-diboryalkenes (**3k**–**n**) with a sole *cis*-selectivity, while a higher temperature and a prolonged reaction time were required (entries 10–13). In the cases of the conjugated enyne **1o** and the α,β-unsaturated alkynyl ester **1p**, the reactions gave the desired products **3o** and **3p** in high yields without reacting with olefin moiety or ester group, but some amounts of the *trans*-adducts **3o′** and **3p′** were obtained which were formed through the thermal isomerization (entries 14 and 15).

Table 2. AuNPore-Catalyzed Diboration of Various Alkynes[a]



1b R^1 = 4-Me-C_6H_4; R^2 = H
1c R^1 = 2-Me-C_6H_4; R^2 = H
1d R^1 = 4-MeO-C_6H_4; R^2 = H
1e R^1 = 2-MeO-C_6H_4; R^2 = H
1f R^1 = 4-F-C_6H_4; R^2 = H
1g R^1 = *c*-$C_6H_{11}CH_2$; R^2 = H
1h R^1 = $THPOCH_2$; R^2 = H
1i R^1 = *n*-C_8H_{17}; R^2 = H
1j R^1 = C_6H_5; R^2 = C_6H_5
1k R^1 = C_6H_5; R^2 = Me
1l R^1 = *n*-C_7H_{15}; R^2 = Me
1m R^1 = *n*-C_3H_7; R^2 = *n*-C_3H_7
1n R^1 = $MeOCH_2$; R^2 = $MeOCH_2$
1o R^1 = C_6H_5; R^2 = (*E*)-CH=CHC_6H_5
1p R^1 = *n*-C_6H_{13}; R^2 = CO_2Me

entry	1	temp (°C)	time (h)	yield[b] (%) (**3** and **3′**)	3:3′[c]
1	**1b**	120	16	87	92:8
2	**1c**	100	16	96	100:0
3	**1d**	100	12	89	82:18
4	**1e**	100	14	98	98:2
5	**1f**	100	12	93	98:2
6	**1g**	120	12	93	98:2
7	**1h**	100	12	73	96:4
8	**1i**	120	40	90	96:4
9[d]	**1j**	100	12	99	100:0
10[d]	**1k**	120	48	80	100:0
11[e,f]	**1l**	140	36	82	100:0
12[d,f]	**1m**	140	48	41	100:0
13[e]	**1n**	100	72	45	100:0
14[d]	**1o**	100	18	98	93:7
15[e]	**1p**	100	16	84	75:25

[a] Reaction conditions: **1b**–**h**, **1j**, **1o**, **1p** (1 mmol), **2a** (1.5 mmol), toluene (2 mL), and AuNPore (2 mol %); **1i**, **1k**–**n** (5 mmol), **2a** (1 mmol), toluene (1 mL), AuNPore (2 mol %). [b] Isolated yield. [c] Ratio determined by ^{1}H NMR. [d] AuNPore (10 mol %) was used. [e] AuNPore (5 mol %) was used. [f] Neat conditions.

To gain further insight into reaction details, we carried out a cross-addition experiment. The reaction of phenylacetylene (**1a**) (1 mmol), B_2pin_2 (**2a**) (1.5 mmol), and B_2hex_2 (**2b**) (1.5 mmol) in the presence of AuNPore (2 mol %) in toluene at 100 °C for 14 h gave a mixture of diboration products in 74% yield; a ratio of **3a**:**3bb**:(**3ab** + **3ba**) was

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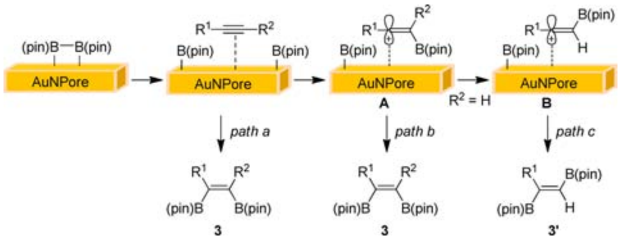
2:1:2 (Scheme S4, Supporting Information), which was determined by mass spectrometry (GC−MS) and ^{1}H NMR analysis (Figure S3, Supporting Information). The formation of the cross-addition products **3ab** and **3ba** suggested that the reaction did not involve the oxidative addition of diborons to Au(0).[15] Further, from the fact that no leaching of gold atoms took place, we thought that the B−B bond of diborons would be cleaved by the solid state of the unsupported AuNPore followed by addition of boron to alkynes to form the 1,2-diborylalkenes. In addition, adding the radical inhibitor 2,6-di-*tert*-butyl-4-methylphenol (BHT) to the AuNPore-catalyzed diboration of **1a** and **2a** did not decrease the rate and yield of **3a**; the yield of **3a** was still 96% after 1.5 h (Scheme S5, Supporting Information). This result implied that the involvement of a radical species was unlikely in the present diboration.[16]

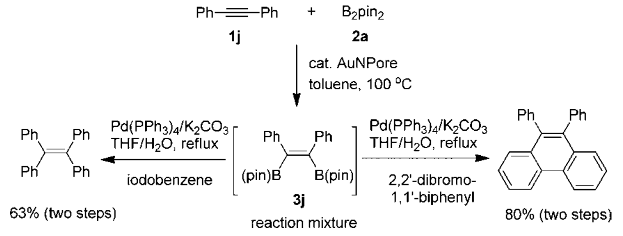
Although the detailed driving force for the cleavage of a B−B bond on the AuNPore surface remains uncertain, on the basis of the experimental observations, a conceivable reaction pathway is shown in Scheme 1. Initially, B_2pin_2 gets absorbed onto the low coordinated Au atoms on the stepped surface of AuNPore. The B−B bond is cleaved on the surface of AuNPore to give [Au−Bpin] species under the reaction conditions. Next, the adsorbed alkyne reacts rapidly with two [Au−Bpin] species either through the simultaneous addition path to form the corresponding *cis*-adduct **3** (path a) or through the stepwise addition (path b), in which the formation of a vinyl cation intermediate is involved. There might exist an interaction between the vinyl cation and the electron-rich Au atoms. In the case of terminal alkyne (R^2 = H), the *trans*-adducts **3′** would be produced through the interaction mode **B** due to the less sterically hindrance between the AuNPore surface and the hydrogen substituent compared to that in the mode **A**, especially for the more stable vinyl cation (path c). This might be the reason why the terminal alkynes **1b** and **1d** having an electron-donating group such as methyl or methoxy at the 4-position of the benzene ring produced increased amounts of *trans*-adducts **3b′** and **3d′** (Table 2, entries 1 and 3). It is noted that the *trans*-diboration of alkynes has been rarely observed previously.[17]

The present heterogeneous catalytic process is favorable for the subsequent one-pot functionalization of the 1,2-diboryl alkene intermediates by simple recovery of AuNPore catalyst (Scheme 2). For example, after conversion of 1,2-diphenylethyne **1j** and B_2pin_2 **2a** into the 1,2-diborylalkene **3j** in the presence of AuNPore catalyst, the reaction mixture was transferred by syringe to the other reaction vessel which was equipped with a mixture of 2,2′-dibromobiphenyl, Pd-catalyst, and base in THF and water solution. The remaining AuNPore catalyst was recovered by a simple washing with acetone for the next use. The Pd-catalyzed double cross-coupling annulation of the reaction mixture gave 9,10-diphenylphenanthrene in 80% yield.[18] Under the similar procedure, 1,1,2,2-tetraphenylethene was obtained in 63% yield through the AuNPore-catalyzed diboration and the subsequent double-Suzuki−Miyaura coupling.

Scheme 1. Plausible Reaction Pathway of the AuNPore-Catalyzed Diboration of Alkynes



Scheme 2. Subsequent Functionalization of 1,2-Diborylalkene **3j** by Recovery of AuNPore Catalyst



In summary, we have demonstrated for the first time an unprecedented catalytic property of the AuNPore on activation of diborons that promotes the direct diboration of alkynes efficiently. The diboration of various terminal and internal alkynes with B_2pin_2 afforded the corresponding 1,2-diborylalkenes in good to high yields with high *cis*-selectivities. Our experimental results indicated that the cleavage of the B−B bond of diborons occurs on the solid state of the AuNPore catalyst without any additives, which leads to the subsequent diboration with alkynes in a heterogeneous process. Further studies are currently underway to understand the origin of this unusual catalytic property of the AuNPore on activation of the B−B bond, and development of new boration reactions catalyzed by the AuNPore is in progress.

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Supporting Information Available. Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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