

Stereoselective Single (Copper) or Double (Platinum) Boronation of Alkynes Catalyzed by Magnesia-Supported Copper Oxide or Platinum Nanoparticles

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Abstract: Copper(II) oxide nanoparticles supported on magnesia have been prepared from Cu^{II} supported on magnesia by hydrogen reduction at 400 °C followed by storage under ambient conditions. X-ray photoelectron spectroscopy of the material clearly shows that immediately after the reduction copper(0)–metal nanoparticles are present on the magnesia support, but they undergo fast oxidation to copper oxide upon contact with the ambient for a short time. TEM images show that the catalytically active CuO/MgO material is formed of well-dispersed copper oxide nanoparticles supported

on fibrous MgO. CuO/MgO exhibits a remarkable catalytic activity for the monoborylation of aromatic, aliphatic, terminal, and internal alkynes, the products being formed with high regio- (borylation at the less substituted carbon) and stereoselectivity (*trans*-configured). CuO/MgO exhibits complete chemoselectivity towards the monoborylation of alkynes in the presence of alkenes. Other metal nanopar-

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ticles such as gold or palladium are inactive towards borylation, but undergo undesirable oligomerization or partial hydrogenation of the C≡C triple bond. In contrast, platinum, either supported on magnesia or on nanoparticulate ceria, efficiently promotes the stereoselective diborylation of alkynes to yield a *cis*-configured diboronate alkene. By using platinum as the catalyst we have developed a tandem diborylation/hydrogenation reaction that gives *vic*-diboronated alkanes from alkynes in one pot.

Introduction

Organoboron compounds are useful organometallic intermediates^[1–5] because they can react to form new carbon–carbon,^[6,7] carbon–nitrogen,^[8] and carbon–oxygen^[9,10] bonds. In view of the widespread use of organoboron compounds in synthesis,^[11,12] the development of general routes for the preparation of these compounds is of general interest.^[13]

In this paper we report on the reaction of phenylacetylene (**1**) with bis(pinacolato)diboron (**2**) as reagent in the presence of copper oxide supported on magnesium oxide (CuO/MgO), which is a highly active catalyst for the chemo- (preference for triple over double bonds), regio- (less substituted boronate), and stereoselective (*trans* isomer) monoborylation of alkynes to give alkenyl boronates. Whereas analogous gold and palladium catalysts show no catalytic activity in this process, we have found that platinum nanoparticles supported on magnesia (Pt/MgO) promote the stereoselec-

tive diborylation of alkynes. These compounds have already been synthesized.^[14,15]

Compared with boranes, the use of boronic acids and boronates as reagents, particularly compound **2**, is advantageous due to the simplicity of the manipulation and the convenient reaction protocol employing these compounds. Bis(pinacolato)diboron is considerably more stable towards oxygen and moisture than other borane analogues that cannot be handled in air due to oxidative and hydrolytic reactions of the B–H bonds.

The use of nanoparticles as heterogeneous catalysts is a current topic of research. Besides noble metal nanoparticles, there is increasing interest in exploiting the catalytic activity of less costly transition metals.^[16,17] In this regard, the use of copper catalysts as substitutes for expensive noble metals is of economic importance. In this report we will show the remarkable contrasting catalytic behavior of CuO/MgO and Pt/MgO, on the one hand, and the differences between these two catalysts and other magnesia-supported metal nanoparticles, on the other.

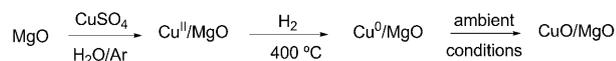
Results and Discussion

Catalysts: MgO is a basic metal oxide that can be used as a support for nanoparticles.^[18] For those reactions requiring basic conditions, the use of MgO can be advantageous, promoting the catalytic activity of the supported sites.

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When a low loading of CuSO₄ was supported on magnesia, a pale-blue solid was obtained. X-ray photoelectron spectroscopy (XPS) confirmed the presence of Cu^{II} on the solid (Scheme 1). Reduction of this surface-exchanged Cu^{II}



Scheme 1. Preparation of CuO/MgO showing the different oxidation states of copper.

could not be effected with NaBH₄ in basic aqueous media due to the higher oxidation potential of copper relative to gold and other noble metals. The copper region of the XP spectrum corresponding to the 2p_{3/2} core levels shows a minor peak corresponding to Cu⁰ (approximately 7%) with a binding energy of 932.2 eV and a major peak arising from Cu^{II} species (approximately 93%) probably anchored to the surface OH groups of the support with a binding energy of 935.4 eV (see Figure 1). However, thermal treatment with

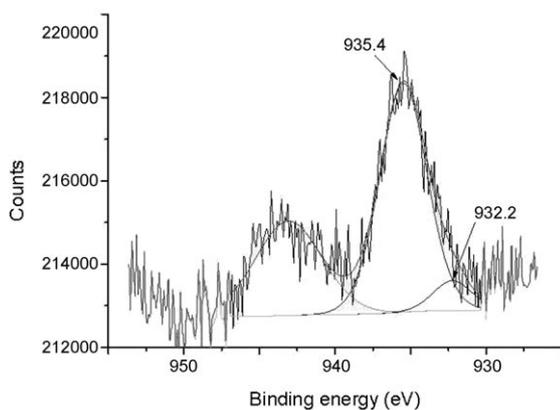


Figure 1. Copper region of the XP spectrum corresponding to the Cu 2p_{3/2} core levels measured for a sample of 1.85 wt% Cu^{II}/MgO.

hydrogen at 400°C effected the reduction of Cu^{II} to Cu⁰, as visually observed by the red color observed in the solid that is characteristic of copper metal (Scheme 1). In situ XPS confirmed that treatment with hydrogen under these conditions led to Cu⁰ metal on the magnesia surface. However, when the freshly prepared Cu⁰/MgO was exposed to ambient conditions, a prompt oxidation of Cu⁰ to CuO took place, as seen by the change in color from red to black and evidenced by XPS (Scheme 1). Figure 2 shows the spectrum of in situ thermo-reduced Cu⁰/MgO (spectrum 1), the deconvolution of which indicates the presence of Cu⁰ (33%) and CuO (67%). The same sample stored under ambient conditions for a few minutes has a different XP spectrum (see Figure 2, spectrum 2), the deconvolution of which indicates that CuO is the prevalent species.

The transmission electron microscopy (TEM) images of the 1.85 wt% Cu^{II}/MgO and 1.85 wt% CuO/MgO samples

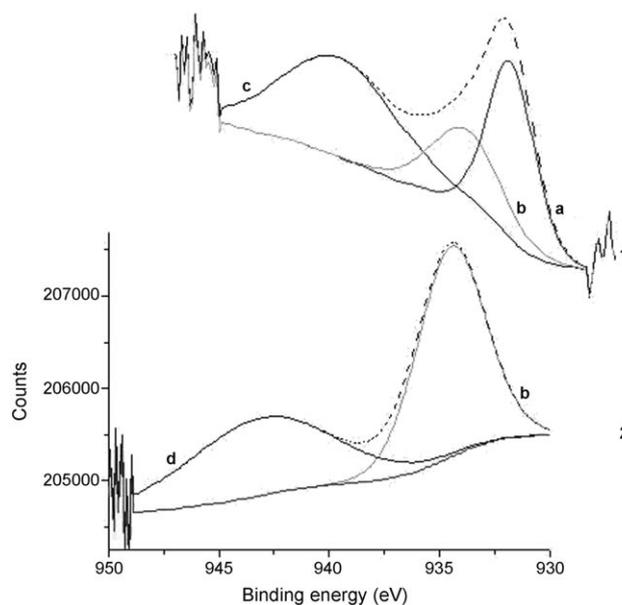


Figure 2. Spectrum 1: Copper region of the XP spectrum corresponding to the Cu 2p_{3/2} core levels of a sample of 1.85 wt% Cu^{II}/MgO reduced in situ with hydrogen at 400°C and the corresponding deconvolution indicating the presence of Cu⁰ with a binding energy of 932.9 eV (plot a) and CuO with a binding energy of 934.7 eV (plot b). Spectrum 2: XP spectrum of the same sample after exposure to ambient conditions for 30 min before recording the XP spectrum. Deconvolution of spectrum 2 shows only the presence of CuO (934.7 eV; plot b). Both spectra show the 2p_{3/2} satellite appearing at 939.40 (plot c) and 942.5 eV (plot d), respectively.

used as catalysts in this study are presented in Figure 3. As can be seen, the fibrous morphology characteristic of MgO is clearly observed in the micrograph recorded for Cu^{II}/MgO with no evidence of the presence of copper oxide particles in this case. On the other hand, the micrograph recorded for CuO/MgO shows that the CuO particles are well dispersed on the surface of the MgO support and that a large number of them are quasi-spherical nanoparticles with a size smaller than 5 nm in diameter.

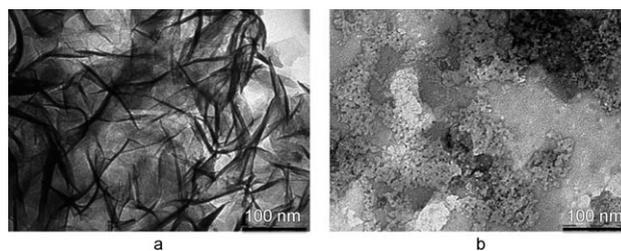


Figure 3. TEM images of a) the 1.85 wt% Cu^{II}/MgO sample and b) the same sample after reduction at 400°C under hydrogen and subsequent exposure to ambient conditions (CuO/MgO).

In this study we also prepared a set of other supported noble metal catalysts. Some of them are commercially available or their preparation has previously been reported in the literature (in the case of Au/CeO₂ and Pt/CeO₂).^[19] For the sake of comparison with CuO/MgO and aimed at estab-

lishing the role of MgO as support, we also prepared Au/MgO, Pd/MgO, and Pt/MgO. The solid catalysts used in this study are presented in Table 1.

TEM analysis of all the samples containing noble metals revealed the presence of homogeneously dispersed metal nanoparticles with narrow size distributions, in good agreement with previous reports.^[19] We noticed, however, that although for Pt/MgO the average particle size was about 3 nm, the average particle size of the Au/MgO sample obtained was 30 nm. Figure 4 shows selected TEM images of Pt/MgO and Au/MgO.

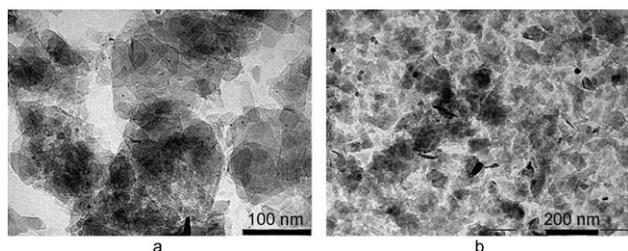


Figure 4. TEM images of a) the 1.37 wt % Pt/MgO and b) the 1.65 wt % Au/MgO catalysts used in this work.

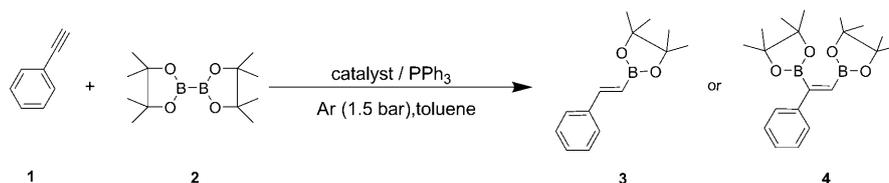
Catalytic mono- or diborylation:

Because of the low stability of Cu⁰/MgO towards the ambient and to obtain reliable catalytic data, most of this study was performed with the Cu^{II}/MgO solid or the CuO/MgO sample resulting from exposure of Cu^{II}/MgO to ambient conditions (see Scheme 1). Cu^{II}/MgO as catalyst was able to promote the monoborylation of phenylacetylene (**1**) by bis(pinacolato)diboronate (**2**) to attain pinacolate boronic acid and cinnamylboronate **3** in various yields depending on the reaction conditions. The product distributions were determined by GC, GC-MS, and ¹H, ¹³C, and ¹¹B NMR spectroscopy. The formation of compound **3** requires the presence of water or another proton donor in the medium.^[20] The results are shown in Table 1. As can be seen, a preliminary control carried out in the presence of equivalent amounts of triphenylphosphine as base but in the absence of any solid showed no reaction (Table 1, entry 1). In contrast,

when Cu^{II}/MgO was added to the reaction mixture, cinnamylboronate **3** was formed even in the absence of triphenylphosphine, although the selectivity towards **3** was low and no full conversion of diboronate **2** was achieved in the absence of triphenylphosphine even after long reaction times (Table 1, entry 2). When both Cu^{II}/MgO and triphenylphosphine were present the reaction proceeded with moderate-to-high selectivity with high conversion (Table 1, entries 3 and 4). We noticed that decreasing the reaction temperature increased the selectivity towards **3** and was accompanied by high diboronate **2** conversion.

We were interested in determining whether the catalytic activity of the copper in Cu^{II}/MgO is similar to that of the sample submitted to reducing conditions. However, as commented upon above, Cu⁰/MgO is sensitive to air and it could be difficult to obtain reproducible data depending on the aging and the extent to which the oxidation of copper has progressed. For this reason, we compared the catalytic activity of Cu^{II}/MgO with that of CuO/MgO (see Scheme 1). The catalytic activity of CuO/MgO relative to that of Cu^{II}/MgO can serve to determine whether the residual population of Cu⁰ are more efficient active sites than Cu^{II}. The results obtained show that CuO/MgO is extremely efficient in promoting the borylation of phenylacetylene, the addition taking place with very high conversions and selectivity to-

Table 1. Conversion of bis(pinacolato)diboron (**2**) and selectivity towards cinnamylboronate (**3**) or cinnamyl-diboronate (**4**) for the reaction of phenylacetylene (**1**) with diboronate **2** using solid catalysts.^[a]



Run	Catalyst	T [°C]	Time [h]	PPh ₃ [mol %]	Conversion ^[b] [%]	Selectivity of 3/4 ^[c]
1	none	160	20	100	0	0:0
2	Cu ^{II} (1.85 wt %)/MgO	160	8	none	50	28:0
3	Cu ^{II} (1.85 wt %)/MgO	160	1.5	5	98	70:7 ^[d]
4	Cu ^{II} (1.85 wt %)/MgO	100	20	5	99	90:0
5	CuO(1.85 wt %)/MgO	100	0.25	5	100	94:0
6	CuO(1.85 wt %)/MgO	45	2.5	5	98	94:0
7	CuI	160	14	5	6	44:0
8	MgO	160	9	5	33	55:0
9	Au(1.65 wt %)/MgO	160	30	5	30	0:0 ^[e]
10	Au(1.5 wt %)/TiO ₂	160	31	5	21	0:0
11	Au(0.72 wt %)/CeO ₂	160	20	5	37	0:0 ^[f]
12	Pd(0.8 wt %)/MgO	160	10	5	99	0:0 ^[g]
13	Pt(1.37 wt %)/MgO ^[h]	160	10	5	97	0:82
14	Pt(1.37 wt %)/MgO	160	1.3	none	92	4:68
15	Pt(1.37 wt %)/MgO	130	4.5	none	99	0:73
16	Pt(0.75 wt %)/CeO ₂	160	0.7	none	99	5:70 ^[i]

[a] Reaction conditions: 0.25 mmol of phenylacetylene (**1**), 0.3 mmol of diborane **2**, 1 mL of toluene, 45 °C, 1.5 bar argon, 4% mol ratio of Cu/ or Au/, or Pd/substrate, and 1% mol ratio platinum/substrate. [b] Conversion based on the disappearance of phenylacetylene (**1**). [c] Selectivity as a percentage relative to compound **3**, except for entries 13–16 which are referenced to compound **4**. [d] The products observed include 3% of the *cis* isomer of **3**. [e] The products observed include 10% styrene together with 20% of undefined oligomers. [f] The products observed include 2% styrene together with 22% of diol and some undefined oligomers. [g] The formation of styrene in a yield of 56% was observed accompanied by oligomers. [h] Platinum/substrate ratio of 4 mol %. [i] The products observed include 3% of diol.

wards monoboronation in very short reaction times and even at very low temperatures (Table 1, entries 5 and 6). Figure 5 shows the time/conversion plot for the reaction of

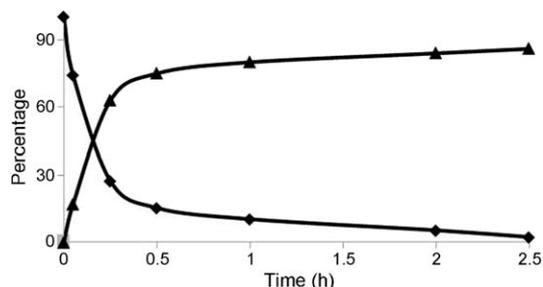


Figure 5. Time/conversion plot for the monoboronation of phenylacetylene (**1**) with diboronate **2** in the presence of 1.85 wt % CuO/MgO. (♦) Disappearance of **2**; (▲) yield of cinnamylboronate **3**. Reaction conditions: 0.25 mmol of phenylacetylene (**1**), 0.3 mmol of diborane **2**, 1 mL of toluene, 45 °C, 1.5 bar argon, 4% mol ratio of Cu/substrate, and 5% mol ratio of triphenylphosphine/substrate.

phenylacetylene (**1**) with diboronate **2** catalyzed by CuO/MgO. The time/conversion plot suggests the occurrence of two concurrent kinetic processes, one faster that fades away at about 75% conversion and another slower that continues operating at longer times. We will comment on the implication of the observation of these two kinetic paths later when discussing the hot filtration tests.

In contrast to the extremely high catalytic efficiency of CuO/MgO, the use of unsupported CuI as catalyst in the presence of triphenylphosphine resulted in a very low diboronate conversion with a low selectivity towards cinnamylboronate **3** (Table 1, entry 7). Another control using MgO as solid catalyst (no copper) in the presence of triphenylphosphine showed moderate diboronate conversion with 55% selectivity towards the coupling product **3** (Table 1, entry 8). No conversion of diboronate **2** took place in the presence of MgO when no triphenylphosphine was added.

It is remarkable that in most of the reaction mixtures with magnesia-supported copper catalysts, compound **3** was obtained with a high level of regio- and stereoselectivity (see Table 1, entry 3 for the least selective case). Cinnamylboronate **3** was obtained in the *trans* configuration, as determined by the coupling constant of the styryl protons in the ¹H NMR spectrum ($J=18.45$ Hz, see the Supporting Information).

The fact that CuO/MgO acts as a heterogeneous catalyst was addressed by performing the hot filtration test and by chemical analysis of the liquid phase. In the hot filtration test, the reaction was started under the usual conditions up to about 18% conversion and then the solid was filtered whilst the reaction mixture was still hot. The clear supernatant was allowed to react up to the final reaction time. Figure 6 provides a comparison of the reactions in the presence of CuO/MgO and in the hot filtration test. It was observed that after filtration the reaction continued to proceed to give 28% yield of **3**. Although the yield from the hot fil-

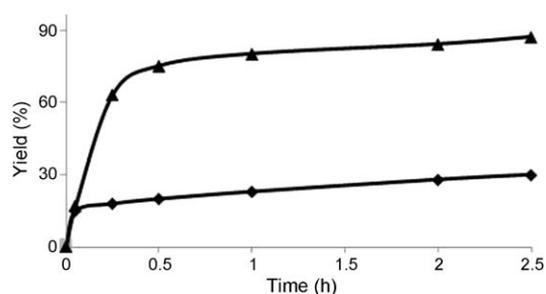


Figure 6. Yield of cinnamylboronate **3** in the presence of 1.85 wt % CuO/MgO (▲) and after hot filtration of the catalyst after 5 min (♦). Reaction conditions: 0.25 mmol of phenylacetylene (**1**), 0.3 mmol of diborane **2**, 1 mL of toluene, 45 °C, 1.5 bar argon, 4% mol ratio of Cu/substrate, and 5% mol ratio of triphenylphosphine/substrate.

tration test is far from the 89% yield achieved in the presence of CuO/MgO, the fact that there is an increase in the conversion of 10% in the absence of the solid indicates that some species leached from the solid to the solution contribute to some extent to the total conversion. In addition, chemical analysis of the liquid phase showed the presence of copper in the liquid in a percentage that corresponds to less than 3% of the total copper content of the catalyst. As commented earlier when discussing the time/conversion plot, it seems that there are two concurrent kinetics, one faster and the other slower. The result of the hot filtration test suggests that the slower process could be due to the copper leached from the solid to the solution and therefore we propose that the faster kinetics probably corresponds exclusively to the heterogeneous catalytic process.

The productivity of CuO/MgO was studied by performing a series of reactions in which the amount of phenylacetylene **1** and diboronate **2** was increased keeping constant the amount of CuO/MgO catalyst. The results are presented in Figure 7. As can be seen, CuO/MgO undergoes a gradual decrease in catalytic activity as larger excesses of phenylacetylene are used for the same amount of catalyst. The decrease in activity can be attributed to the poisoning of the CuO/MgO catalyst by the pinacolate borate ester formed as a byproduct of the reaction.

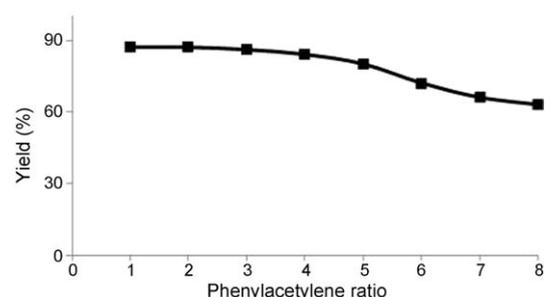


Figure 7. Yield of cinnamylboronate **3** after the catalytic process. Reaction conditions: 0.25 mmol of phenylacetylene (**1**) increased stepwise up to a factor of 8, 0.3 mmol of diboronate ester **2** increased stepwise up to a factor of 8, 1.5 mL of toluene, 45 °C, 1.5 bar argon, 34 mg CuO/MgO, and 5% mol ratio of triphenylphosphine/substrate.

We were interested in determining whether the catalytic activity of the copper-promoted borylation of alkynes is also observed for other metals and particularly whether gold, palladium, and platinum also promote the borylation reaction. Therefore we performed the reaction of phenylacetylene (**1**) with diboronate **2** in the presence of a series of supported metal nanoparticles with different metals and supports. The results are given in Table 1 (see entries 9–16). It can be seen that gold nanoparticles supported on magnesia, titania, or ceria did not lead to the unsaturated organoboronate. The low conversions of phenylacetylene observed at long reaction times using gold as the catalyst is a result of some oligomerization together with the formation of a very minor amount of styrene. We noticed, however, that the three gold catalysts were very different in terms of particle size distribution. Whereas in the Au/CeO₂ sample prepared by us^[21] and in the commercial Au/TiO₂ (World Gold Council, reference A catalyst) gold is present as small nanoparticles with an average size of about 5 nm, in the case of Au/MgO TEM images revealed that the average particle size was 30 nm (see Figure 4). In gold catalysis it is a well-established fact that catalytic activity decreases as the average particle size increases^[22,23] and therefore, based exclusively on this parameter, it can be expected that Au/MgO would be the least active sample of the series.

In the case of Pd/MgO, a similar product distribution to that found for the gold catalyst, that is, styrene and some oligomers, was also observed but with an almost complete conversion of the starting phenylacetylene (Table 1, entry 12 and footnote g). These results can be interpreted assuming that gold and palladium do not interact with bis(pinacolato)-diboron and that they act as oligomerization/hydrogenation catalysts of phenylacetylene, particularly in the case of palladium.

Totally different behavior was observed for the supported platinum catalyst irrespective of the presence or absence of triphenylphosphine (Table 1, entries 13–16). The most important feature of the use of platinum as catalyst is the formation of the diboronate alkene **4** as the major product and not the monoboronate compound **3**. It has been reported in the literature that tetrakis(triphenylphosphino)platinum(0) complexes act as homogeneous catalysts for the diboronation of alkynes.^[24,25] In our case, we have reproduced the reported diboronation of phenylacetylene using [Pt(PPh₃)₄] as homogenous catalyst and observed the same reaction product as when using Pt/MgO as the catalyst. Interestingly, the 1,1-diboronate isomer of compound **4** was undetectable although it had also been observed in the homogenous catalytic reaction, which indicates the remarkable regioselectivity of Pt/MgO. However, we noticed that in the absence of PPh₃, the presence of very small, but detectable, amounts of the monoboronated alkene **3** were also observed with Pt/MgO or Pt/CeO₂ as the catalyst (Table 1, entries 14–16). The time/conversion plot obtained by using Pt/MgO as heterogeneous catalyst (Figure 8) shows that the diboronated compound **4** is a primary reaction product and does not arise from a sequential borylation of the monoboronated

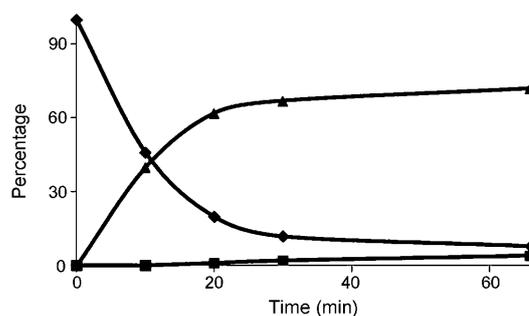


Figure 8. Time/conversion plot for the diboronation of phenylacetylene (**1**) with diboronate **2** in the presence of 1.37 wt% Pt/MgO. (◆) Disappearance of **1**; (■) yield of cinnamylboronate **3**; (▲) yield of styryldiboronate **4**. Reaction conditions: 0.25 mmol of phenylacetylene (**1**), 0.3 mmol of diborane **2**, 1 mL of toluene, 160 °C, 1.5 bar argon, and 1% mol ratio of Pt/substrate.

compound **3**. As with [(Ph₃P)₄Pt⁰] in the homogeneous phase, the diboronated product **4** is formed in the presence of Pt/MgO in a stereoselective manner, the two boronate groups being in a *cis* configuration. With platinum nanoparticles as catalyst we also observed that in addition to MgO, ceria is also a suitable support (Table 1, entry 16), giving essentially the same results as when using MgO as the support.

Scope of the catalytic borylation of alkynes: The scope of the mono- (using copper as catalyst) and diboronation (using platinum as catalyst) reactions was expanded by performing the borylation of other aromatic and aliphatic, terminal and internal alkynes. The results are summarized in Table 2. As can be seen, high selectivity at high conversion was attained in almost every case. Importantly, the same features as those commented upon above for phenylacetylene were also observed for the other alkynes. Thus, in the case of Cu^{II}/MgO, triphenylphosphine even in small amounts was necessary to form the monoborylated product with high selectivity, the reaction occurring with high regio- and stereoselectivity. Also, as in the case of phenylacetylene, the reduced CuO/MgO sample exhibits far more catalytic activity than the ambient-equilibrated Cu^{II}/MgO sample (Table 2, entries 4, 5, 9, 10, 15, 16, 20, 21, and 26). As an example, Figure 9 shows the time/conversion plot for the boronation of diphenylacetylene (**11**) using CuO/MgO as the catalyst. The results have been attributed to the presence of a residual population of Cu⁰ species in the sample as observed by XPS.

With Pt/MgO as the catalyst, the product formed was almost exclusively the diborylated alkene, which was formed even in the absence of triphenylphosphine. Again, the time/conversion plots show that the diborylated compounds were formed as primary products and not derived from monoborylated products. As an example, Figure 10 shows the time/conversion plot for the diborylation of 4-octyne (**18**) using Pt/MgO as the catalyst.

The reaction appears to be general in scope for all the alkynes tested. For both MgO-supported catalysts, internal,

Table 2. Conversion and selectivity towards the mono- or diboronation product for the reaction of various alkynes and diboronate **2** catalyzed by supported copper or platinum catalysts.^[a]

Run	Substrate	Catalyst	T [°C]	Time [h]	PPh ₃ [mol %]	Conversion ^[b] [%]	Selectivity [%]
1		none	160	20	100	0	–
2		Cu ^{II} (1.85 wt %)/MgO	160	3	5	95	 6: 70 7: 10
3		Cu ^{II} (1.85 wt %)/MgO	100	3	5	100	6: 89 7: 3
4		CuO(1.85 wt %)/MgO	100	1	5	95	6: 92
5		CuO(1.85 wt %)/MgO	45	2	5	95	6: 93
6		Pt(1.37 wt %)/MgO ^[c]	160	1.5	5	100	 7: 69
7		Cu ^{II} (1.85 wt %)/MgO	160	5	5	96	 9: 68 cis isomer: 5 10: 15
8		Cu ^{II} (1.85 wt %)/MgO	100	10	5	99	9: 80 cis isomer: 5 10: 9
9		CuO(1.85 wt %)/MgO	100	0.06	5	95	9: 82 cis isomer: 10 10: 2
10		CuO(1.85 wt %)/MgO	45	0.5	5	98	9: 83 cis isomer: 7 10: 3
11		Pt(1.37 wt %)/MgO	160	1.2	none	98	 10: 90
12		Pt(1.37 wt %)/MgO	130	2	none	100	10: 92
13		Cu ^{II} (1.85 wt %)/MgO	160	2	5	100	 12: 94

Table 2. (Continued)

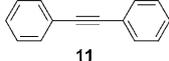
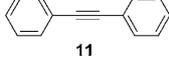
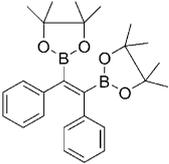
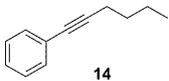
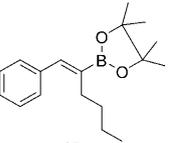
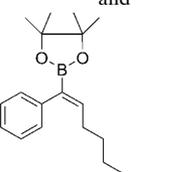
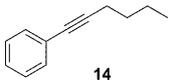
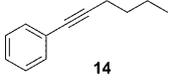
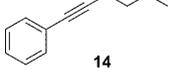
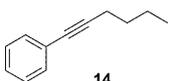
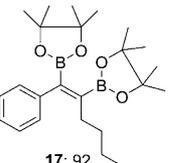
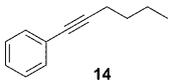
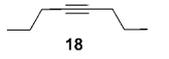
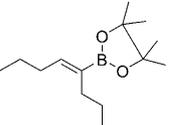
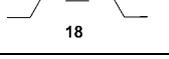
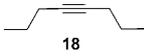
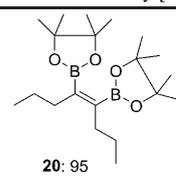
Run	Substrate	Catalyst	<i>T</i> [°C]	Time [h]	PPh ₃ [mol %]	Conversion ^[b] [%]	Selectivity [%]
14	 11	Cu ^{II} (1.85 wt %)/MgO	100	7	5	99	12: 95
15	 11	CuO(1.85 wt %)/MgO	100	1.2	5	100	12: 97
16	 11	CuO(1.85 wt %)/MgO	45	1.5	5	99	12: 97
17	 11	Pt(1.37 wt %)/MgO	160	1	5	100	 13: 91
18	 14	Cu ^{II} (1.85 wt %)/MgO	160	4	5	99	 15:90 and  16: 7
19	 14	Cu ^{II} (1.85 wt %)/MgO	100	20	5	100	15: 93 16: 4
20	 14	CuO(1.85 wt %)/MgO	100	1	5	99.7	15: 95 16: 3
21	 14	CuO(1.85 wt %)/MgO	45	6	5	99	15: 94 16: 3
22	 14	Pt(1.37 wt %)/MgO	160	2	none	100	 17: 92
23	 14	Pt(1.37 wt %)/MgO ^[d]	160	1	7	100	17: 94
24	 18	Cu ^{II} (1.85 wt %)/MgO	160	3	5	99	 19: 56 20: 34
25	 18	Cu ^{II} (1.85 wt %)/MgO	100	5	5	95	19: 75 20: 17
26	 18	CuO(1.85 wt %)/MgO	100	3	5	99	19: 80 20: 12

Table 2. (Continued)

Run	Substrate	Catalyst	T [°C]	Time [h]	PPh ₃ [mol %]	Conversion ^[b] [%]	Selectivity [%]
27		Pt(1.37 wt %)/MgO	160	1	none	99	

[a] Reaction conditions: alkyne 0.25 mmol, compound **2** 0.3 mmol, toluene 1 mL, argon pressure 1.5 bar at the indicated reaction temperature, copper/substrate ratio 4 mol % and platinum/substrate ratio 1 mol %. [b] Conversion based on the disappearance of alkyne. [c] 4 % mol ratio of platinum/substrate. [d] 4 % mol ratio of platinum/substrate.

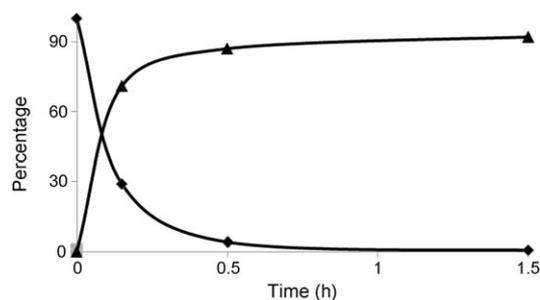


Figure 9. Time/conversion plot for the monoborylation of diphenylacetylene (**11**) with diboronate **2** using 1.85 wt % Cu⁰/MgO as the catalyst. (◆) Disappearance of **11**; (▲) yield of borylalkene **12**. Reaction conditions: 0.25 mmol of diphenylacetylene, 0.3 mmol of diborane **2**, 1 mL of toluene, 45 °C, 1.5 bar argon, 4 % mol ratio of Cu/substrate, and 5 % mol ratio of triphenylphosphine/substrate.

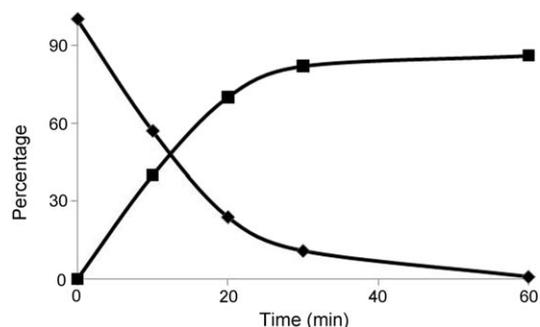


Figure 10. Time/conversion plot for the diboronation of 4-octyne (**18**) with **2** in the presence of 1.37 wt % Pt/MgO. (◆) Disappearance of **18**; (■) yield of 1,2-bis(boryl)alkene **20**. Reaction conditions: 0.25 mmol of 4-octyne; 0.3 mmol of **2**; 1 mL of toluene, temperature, 160 °C, 1.5 bar argon, and 1 % mol ratio of Pt/substrate.

external, aliphatic as well as aromatic alkynes reacted with high conversion and remarkable selectivity. Only in the case of butyl(phenyl)acetylene (**14**) was the presence of a minor percentage of the 1-phenyl-1-boryl regioisomer observed (Table 2, entries 18–21). This is understandable considering that the difference in stability of the two isomeric 2- (preferential) and 1- (minor) monoborylated products should be smaller in this case.

Chemoselectivity of the monoborylation of alkynes over alkenes: It was interesting to ascertain the chemoselectivity of the monoborylation of alkynes over alkenes. To address this we performed a competitive borylation of phenylacetylene in the presence of styrene using various amounts of triphenylphosphine. The results shown in Table 3 indicate that phenylacetylene undergoes a clean transformation to compound **3** whereas no conversion of styrene was observed in this experiment. Figures 11 and 12 show the time/conversion plots for the competitive borylation of phenylacetylene and

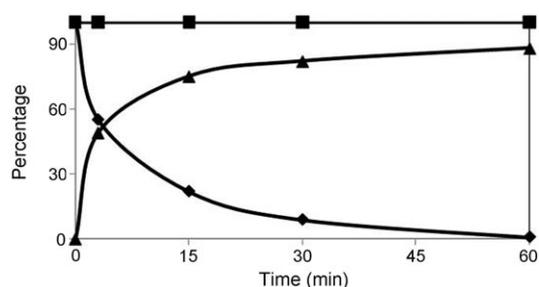


Figure 11. Time/conversion plot for the competitive boronation of phenylacetylene and styrene with diboronate **2** in the presence of 1.85 wt % CuO/MgO. (◆) Disappearance of phenylacetylene, (■) percentage of styrene; (▲) yield of 1-borylalkene **3**. Reaction conditions: 0.25 mmol of phenylacetylene, 0.25 mmol of styrene, 0.3 mmol of diborane **2**, 1 mL of toluene, 45 °C, 1.5 bar argon, 4 % mol ratio of Cu/substrate, and 5 % mol ratio of PPh₃/substrate.

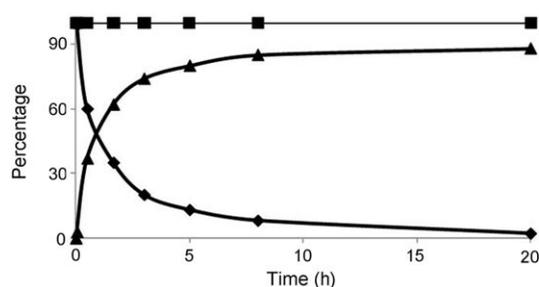
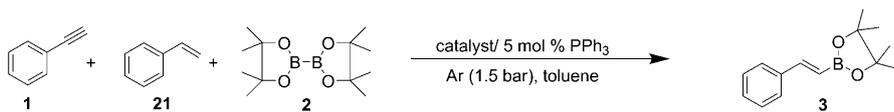


Figure 12. Time/conversion plot for the competitive boronation of phenylacetylene and styrene with diboronate (**2**) in the presence of 1.85 wt % Cu^{II}/MgO. (◆) Disappearance of phenylacetylene; (■) percentage of styrene; (▲) yield of 1-borylalkene **3**. Reaction conditions: 0.25 mmol of phenylacetylene, 0.25 mmol of styrene, 0.3 mmol of diborane **2**, 1 mL of toluene, 45 °C, 1.5 bar argon, 4 % mol ratio of Cu/substrate, and 5 % mol ratio of PPh₃/substrate.

Table 3. Competitive boronation of phenylacetylene (**1**) and styrene (**21**) with **2** (1 equiv) using supported copper catalysts.^[a]



Run	Catalyst	Time [h]	T [C°]	Conversion [%] 	Conversion [%] 	Selectivity ^[b] [%]
1	Cu ^{II} (1.85 wt %)/MgO	1	160	100	3	75 ^[c]
2	Cu ^{II} (1.85 wt %)/MgO	2	100	100	0	93
3	Cu ^{II} (1.85 wt %)/MgO	20	45	98	0	94
4	CuO(1.85 wt %)/MgO	1	45	99	0	95

[a] Reaction conditions: 0.25 mmol of compound **1**, 0.25 mmol of compound **21**, 0.3 mmol of compound **2**, 1 mL of solvent, 1.5 bar argon, 4% mol ratio copper/substrate, and 4% mol ratio PPh₃/substrate mol ratio. [b] Selectivity towards compound **3**. [c] The products observed include 4% of the *cis* isomer **3** together with 10% of undefined oligomers.

styrene by bis(pinacolato)diboron in the presence of 1.85 wt % CuO/MgO and Cu^{II}/MgO as catalysts, respectively.

Reaction mechanism: Because the products obtained with CuO/MgO and Pt/MgO were different, it is proposed that the reactions with the different metals occur by different mechanisms. Although these mechanisms would be expected to have some similarities, there should be some differences due to differences in the coordination ability of copper and platinum.

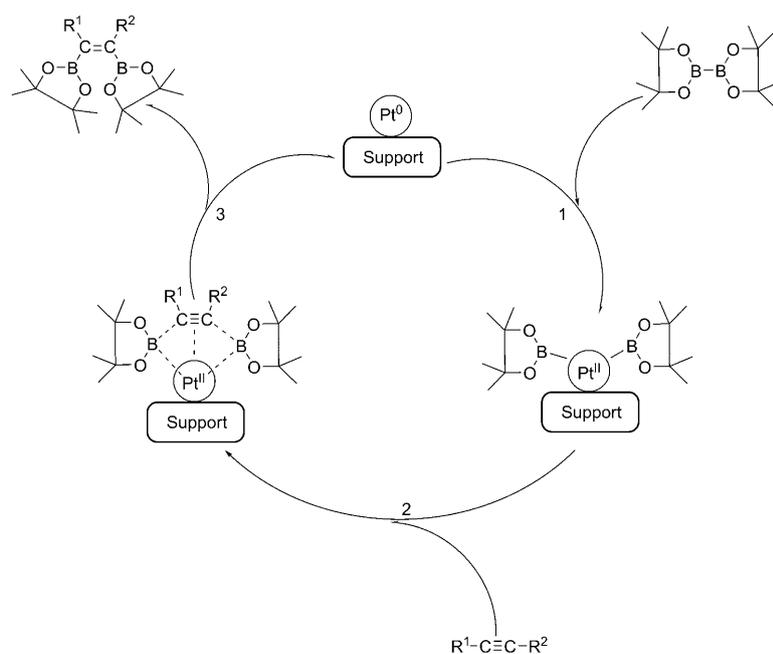
As commented upon earlier, the diboronation of aromatic alkynes has already been reported with [Pt(PPh₃)₄] as a homogenous catalyst.^[24,25] In this case the proposed reaction mechanism was strongly supported by the characterization of a platinum diboronate intermediate that provided evidence for the insertion of platinum(0) into the B–B bond of the bis(pinacolato)diborane (analogous to step 1 in Scheme 2). Based on the firm characterization of this intermediate, a mechanism involving nucleophilic attack of the C≡C triple bond of the alkyne on the Pt–B bonds of the intermediate (step 2 in Scheme 2) was proposed. A similar step has also been proposed to rationalize the formation of compound **4** in homogenous catalysis.^[25] Herein, considering that the reaction described by us is the heterogeneous analogue of the homogenous process and that identical products are formed, an analogous mechanism is pro-

posed. In this mechanism the active sites are the platinum atoms of the metal nanoparticles on the solid surface. Scheme 2 summarizes the proposed mechanism.

Because the supported copper catalyst also leads to C–B bond formation but with the addition of only one (pinacolato)boron unit, the reaction mechanism should have similarities and differences with the case of platinum as catalyst. It is particularly relevant that copper requires the assistance of triphenylphosphine as promoter. To understand the role

of PPh₃ we undertook a ³¹P and ¹¹B NMR spectroscopic study to determine whether a Lewis acid (boron)/base (phosphorous) adduct is formed when the two compounds are in solution. Previous work in the literature has already reported the formation of adducts when diboron compounds are in contact with bases, including phosphines.^[26,27]

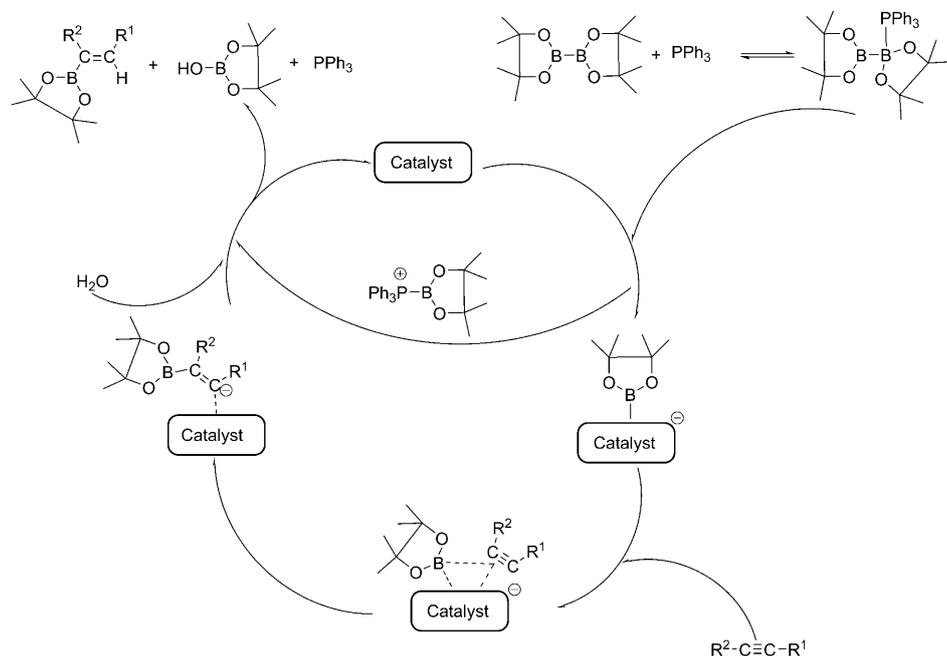
From the shift in the value of δ of PPh₃ in the ³¹P NMR spectrum in the absence and presence of diborane **2** from –5.5 to 24.73 ppm it can be deduced that the expected acid–base adduct is formed. Similar chemical shifts have been reported for B₂–phosphine adducts.^[28] The formation of this adduct was also observed by ¹¹B NMR spectroscopy through the shift in the boron signal from 29.8 to 30.70 ppm. An additional small peak observed in the ¹¹B NMR spectrum at



Scheme 2. Proposed mechanism for the diborylation of alkynes in the presence of platinum catalysts.

21.84 ppm can be attributed to the formation of pinacolboric acid or to some B_2pin_3 as reported previously.^[29] In any case, the peak at 21.84 ppm is significantly less intense than the peak at 30 ppm attributable to the B_2-PPh_3 adduct. However, in the ^{11}B NMR spectra, the peaks are considerably closer and broader than in the ^{31}P NMR spectra due to the nuclear quadrupole of boron, making it less informative. The Supporting Information contains the corresponding ^{31}P and ^{11}B NMR spectra of the adduct formed between PPh_3 and $(pin)_2B_2$.

Based on this Lewis acid–base adduct activating the boron–boron bond and the analogy between the platinum- and copper-catalyzed boronation reactions, the mechanism illustrated in Scheme 3 is proposed for the boronation reaction using Cu^{II}/MgO or CuO/MgO as catalyst. As can be



Scheme 3. Mechanism proposed for the monoboronation of alkynes catalyzed by Cu^{II}/MgO or CuO/MgO assisted by PPh_3 .

seen from Schemes 2 and 3, the main differences between the mechanisms are the PPh_3 -assisted cleavage of the B–B bond in the copper-catalyzed reaction and one of the boron units strongly interacting with the phosphorus throughout the reaction and finally forming a boric ester or borate due to the reaction with water. The formation of pinacolboric acid as a final byproduct in the monoboronation in the presence of Cu/MgO was ascertained by ^{11}B NMR spectroscopy; in addition to the peak at 29.54 ppm corresponding to compound **3**, another peak at 21.85 ppm is observed at the end of the reaction that can be attributed to this byproduct. The ^{11}B NMR spectrum of the mixture corresponding to the formation of compound **3** at the end of the reaction can be found in the Supporting Information. According to the reac-

tion mechanism, the formation of the monoboronated product requires a proton source^[14] (and OH^- to split the boronate–phosphine adduct).

Tandem diborylation/hydrogenation catalyzed by Pt/MgO:

Because supported platinum is a typical hydrogenation catalyst, we have devised a tandem reaction in which the diborylation of phenylacetylene (**1**) and 1-octyne (**8**) to form the corresponding diborylated alkenes **4** and **10** is coupled in a single pot/single catalyst system with subsequent hydrogenation of the resulting alkenes to form diborylated alkanes. The reaction and the results obtained are summarized in Table 4.

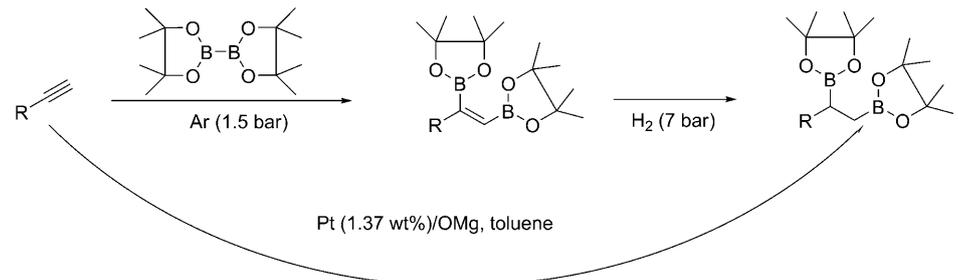
The tandem process was successfully achieved by performing first the diborylation step under argon atmosphere and then by using a hydrogen atmosphere for the hydrogenation step. Control experiments in which the two steps were performed under hydrogen atmosphere (rather than argon followed by hydrogen) showed that under these conditions hydrogenation of the $C\equiv C$ triple bond prevails and occurs faster than diborylation. It was also observed that the rate of hydrogenation of the starting alkynes is much higher than the rate of hydrogenation of diboronated alkenes. We attribute the lower rate of hydrogenation of the diboronated alkenes with respect to the corresponding alkynes to the steric encumbrance around the $C=C$ double bond due to the presence of the bulky boronated substituents that must slow down the hydrogenation of alkenes **4** and **10** relative to the hydrogenation of alkynes **1** and **8**.

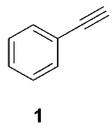
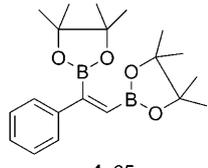
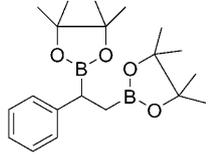
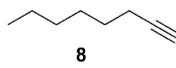
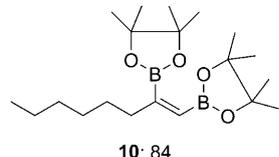
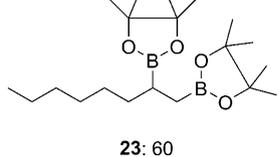
As indicated in footnote b of Table 4, starting from 1-octyne (**8**), a certain degree of $C=C$ bond migration (10%) was observed as a result of the undesirable $C=C$ isomerization promoted by hydrogen. In any case, the data in Table 4 illustrates that it is possible to perform the two catalytic steps in a one-pot reaction using Pt/MgO as a single catalyst.

Conclusion

In this paper we have reported that magnesia-supported Cu^{II} or copper oxide nanoparticles exhibit a unique regio- and stereoselectivity in the catalyzed monoborylation of alkynes with bis(pinacolato)diboron assisted by triphenylphos-

Table 4. Tandem synthesis of 1,2-bis(boryl)alkanes starting from the corresponding alkynes by a two-step, one-pot process using Pt/MgO as catalyst.^[a]



Substrate	<i>P</i> [bar] (gas)	<i>T</i> [°C]	Time [h]	Product: Yield ^[b] [%]	Conversion [%]	Selectivity [%]
	1.5 (Ar)	160	1.3	 4: 65	92 ^[c]	68
	7 (H ₂)	160	7	 22: 60	97	66
1	1.5 (Ar)	130	4.5	4: 72	98	74
	7 (H ₂)	130	27	22: 47	64	70
	1.5 (Ar)	130	4	4: 70	90	63
	7 (H ₂)	130	13	22: 64	93	65
	1.5 (Ar)	160	1.2	 10: 84	98 ^[c]	88
	7 (H ₂)	160	15	 23: 60	92	64
8	1.5 (Ar)	130	2	10: 91	100	91
	7 (H ₂)	130	20	23 ^[d] : 66	70	69
8 ^[d]	1.5 (Ar)	130	2	10: 89	100	89
	7 (H ₂)	130	0.5	23 ^[d] : 64	99	65

[a] Reaction conditions: 0.25 mmol of alkyne, 0.3 mmol bis(pinacolato)diboron, 1 mL of toluene, and 1% mol ratio platinum/substrate. [b] Isolated yields based on alkyne. [c] Conversion based on the disappearance of alkyne. [d] Approximately 10% of diboronated isomers were also observed. [e] 2% mol ratio of platinum/substrate.

phine. The process is general for aromatic and aliphatic, terminal as well internal alkynes and occurs with high chemoselectivity for the C≡C triple bond versus the C=C double bond. Supported platinum exhibits higher catalytic activities even in the absence of triphenylphosphine, but the products formed are the bis-boronated alkenes. With platinum, ceria is also a suitable support. The use of platinum has led to the development of a tandem diborylation/hydrogenation reaction to form diborylated alkanes.

Experimental Section

Catalyst preparation: Nanopowder ceria was obtained from Sigma-Aldrich Company. Cu^{II} was deposited onto magnesium oxide at room temperature (23 °C) by vigorous stirring of an aqueous suspension (20 mL of deionized water at pH 6.7) of MgO (2 g) containing CuSO₄·5H₂O (203 mg) for 4 h under a flow of argon (0.5 mL min⁻¹). The solid was then filtered, washed with deionized water (2.5 L), acetone (100 mL), and diethyl ether (20 mL), and finally dried under vacuum at 100 °C for 16 h. The final copper content was 1.85 wt %, as determined by quantitative atomic absorption analysis.

Cu⁰(1.85 wt %)/MgO was obtained by calcination of Cu^{II}(1.85 wt %)/MgO at 400 °C for 5 h under a flow of H₂ (80 mL min⁻¹). Storage of Cu⁰(1.85 wt %)/MgO under ambient conditions renders CuO(1.85 wt %)/MgO.

Using magnesia as support, Pt/MgO, Au/MgO, and Pd/MgO were also prepared. These catalysts were obtained by impregnation of commercial MgO (1 g, calcined at 400 °C for 4 h) with a deionized aqueous solution (13 mL) of [H₂PtCl₆]·6H₂O (54 mg; Aldrich), [HAuCl₄] (42 mg; Alfa Aesar), or PdCl₂ (23 mg, Aldrich, purum, 60% palladium content), respectively. The slurry was stirred for 15 h at room temperature and then all the liquid was evaporated and the solid was dried at 100 °C for 2 h and reduced with 1-phenylethanol at 433 K for 3 h. The catalyst was then filtered, washed, and dried at 100 °C for 12 h. The final platinum, gold, and palladium contents were found to be 1.37, 1.65, and 0.8 wt %, respectively, by atomic absorption analysis.

Nanoparticulate ceria was obtained as reported previously^[30] by hydrolysis of cerium nitrate aqueous solutions at pH 5 using ammonia as base. The colloid was purified by dialysis. Gold was deposited on the nanoparticulate cerium oxide by the following procedure: A solution of [HAuCl₄]-3H₂O in deionized water (50 mL) was adjusted to pH 10 by the addition of a solution of 0.2 M NaOH. Once the pH value was stable, the solution was added to a slurry containing colloidal CeO₂ (10 g) in H₂O (80 mL). After adjusting the pH with 0.2 M NaOH, the slurry was left to stir vigorously for 18 h at room temperature. The Au/CeO₂ solid was then filtered and exhaustively washed with distilled water until no traces of chloride were detected by the AgNO₃ test. The catalyst was dried at room temperature under vacuum. Finally, the Au/CeO₂ was activated by reduction by pouring the solid into boiling 1-phenylethanol for 2 h. After recovering the solid, washing, and drying, the solid was ready to be used as a catalyst. The total gold content of the final catalyst was 0.72 %, as determined by chemical analysis. The average particle size

of the gold nanoparticles, as determined by statistical analysis of a sufficiently large number of particles, was 3.97 nm.

Also, by using nanoparticulate ceria as support, Pt/CeO₂ was prepared by impregnation of CeO₂ (2 g) with a solution of [H₂PtCl₆]-6H₂O (Aldrich) in H₂O (milliQ; 5 mL). The slurry was stirred for 3 h at room temperature, then all the liquid was evaporated, and the solid was dried at 100°C overnight and reduced with 1-phenylethanol at 160°C for 3 h. The catalyst was then washed, filtered, and dried at 100°C for 12 h. The final platinum content was found to be 0.7 wt% by atomic absorption analysis.

The Au/TiO₂ catalyst consists of 1.5 wt% gold on TiO₂ and was supplied by the World Gold Council (reference catalysts, Type A).

Catalytic experiments: All the reactants used in this study were obtained from Sigma–Aldrich with a purity greater than 95%. Catalytic experiments were performed in reinforced-glass reactors equipped with temperature and pressure control. For each reaction, a 1 mL mixture of reactants and solvent was placed in a reactor (2.5 mL capacity) together with the appropriate amount of catalyst. The reactions were carried out at the indicated temperature and at 1.5 bar of argon or 7 bar of hydrogen. The course of the reaction was determined by analyzing aliquots (40 µL) from the reaction mixture and injecting them into a GC. Conversions and yields were estimated by using dodecane as an internal standard. Conversions and yields were also determined by ¹H NMR spectroscopy from the integrals of the signals corresponding to the products and comparing them with those of (Me₃Si)₂O added as an internal standard.

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- [1] H. C. Brown in *Hydroboration*, New York, Wiley, **1962**.
- [2] H. C. Brown, *Boranes in Organic Chemistry*, Cornell University Press, Ithaca, **1972**.
- [3] H. C. Brown, *Boranes in Organic Synthesis via Boranes*, Wiley, New York, **1975**.
- [4] C. M. Vogels, S. A. Westcott, *Curr. Org. Chem.* **2005**, *9*, 687–699.
- [5] T. A. Boebel, J. F. Hartwig, *J. Am. Chem. Soc.* **2008**, *130*, 7534–7535.
- [6] S. R. Chemler, D. Trauner, S. J. Danishefsky, *Angew. Chem.* **2001**, *113*, 4676–4701; *Angew. Chem. Int. Ed.* **2001**, *40*, 4544–4568.

- [7] M. Rubina, M. Rubin, V. Gevorgyan, *J. Am. Chem. Soc.* **2003**, *125*, 7198–7199.
- [8] E. Fernandez, K. Maeda, M. W. Hooper, J. M. Brown, *Chem. Eur. J.* **2000**, *6*, 1840–1846.
- [9] T. Hayashi, Y. Matsumoto, Y. Ito, *Tetrahedron: Asymmetry* **1991**, *2*, 601–612.
- [10] J. M. Brown, D. I. Hulmes, T. P. Layzell, *J. Chem. Soc. Chem. Commun.* **1993**, 1673–1674.
- [11] N. Miyaura in *Organoboron Compounds, Vol. 219*, **2002**, Springer, Heidelberg, pp. 11–59.
- [12] A. Suzuki, *J. Organomet. Chem.* **1999**, *576*, 147–168.
- [13] A. Leyva, X. Zhang, A. Corma, *Chem. Commun.* **2009**, 4947–4949.
- [14] K. Takahashi, T. Ishiyama, N. Miyaura, *J. Organomet. Chem.* **2001**, *625*, 47–53.
- [15] R. L. Thomas, F. E. S. Souza, T. B. Marder, *Dalton Trans.* **2001**, 1650–1656.
- [16] K. Kohnno, K. Nakagawa, T. Yahagi, J. C. Choi, H. Yasuda, T. Sakakura, *J. Am. Chem. Soc.* **2009**, *131*, 2784–2785.
- [17] S. Prateetongkum, I. Jovel, R. Jackstell, N. Vogl, C. Weckbecker, M. Beller, *Chem. Commun.* **2009**, 1990–1992.
- [18] H. Hattori, *Chem. Rev.* **1995**, *95*, 537–558.
- [19] A. Abad, C. Almela, A. Corma, H. Garcia, *Chem. Commun.* **2006**, 3178–3180.
- [20] Note: According to the supplier the water content of toluene is 0.05%.
- [21] A. Corma, H. Garcia, *Chem. Soc. Rev.* **2008**, *37*, 2096–2126.
- [22] M. Haruta, *Catal. Today* **1997**, *36*, 153–166.
- [23] A. Abad, A. Corma, H. Garcia, *Chem. Eur. J.* **2008**, *14*, 212–222.
- [24] T. Ishiyama, N. Matsuda, N. Miyaura, A. Suzuki, *J. Am. Chem. Soc.* **1993**, *115*, 11018–11019.
- [25] T. Ishiyama, N. Matsuda, M. Murata, F. Ozawa, A. Suzuki, N. Miyaura, *Organometallics* **1996**, *15*, 713–720.
- [26] R. E. K. Depoy, *Inorg. Chem.* **1985**, *24*, 2871–2872.
- [27] P. Nguyen, C. Y. Dai, N. J. Taylor, W. P. Power, T. B. Marder, N. L. Pickett, N. C. Norman, *Inorg. Chem.* **1995**, *34*, 4290–4291.
- [28] W. P. Power, *J. Am. Chem. Soc.* **1995**, *117*, 1800–1806.
- [29] M. A. Salomon, T. Braun, A. Penner, *Angew. Chem.* **2008**, *120*, 8999–9003; *Angew. Chem. Int. Ed.* **2008**, *47*, 8867–8871.
- [30] J. Y. Chanecching, J. Chane-Ching in *Cerium Oxide Prod Easily Dispersible in Water to Form Stable Sols*, Rhone Poulenc Specialites Chim, Rhone-Poulenc Spec, City, **1987**.

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