

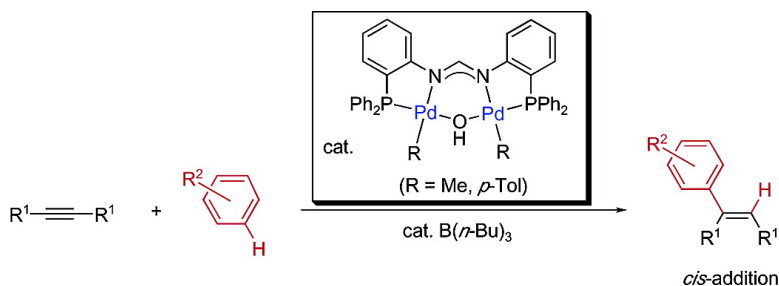
Communication

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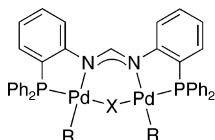
Stereoselective *cis*-Addition of Aromatic C–H Bonds to Alkynes Catalyzed by Dinuclear Palladium Complexes

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The catalytic C–C bond forming reaction via C–H bond activation by transition metal complexes is one of the most attractive subjects in synthetic organic chemistry,¹ especially the addition of C–H to unsaturated bonds,^{1e} which is an ideal atom economical process.² Although many addition reactions of ortho and peri C–H bonds of arenes with directing substituents to alkenes and alkynes via chelation-assisted C–H activation have recently been reported by several groups,^{3,4} the addition of simple arenes via direct C–H activation remains rare. Rhodium-catalyzed photochemical reactions of benzene with alkenes afford alkylbenzenes along with alkenylbenzenes.⁵ Recently, iridium complexes were reported to catalyze anti-Markovnikov hydroarylation of unactivated alkenes with unactivated arenes with good selectivity.⁶ Palladium acetate also provides efficient hydroarylation of activated alkenes in trifluoroacetic acid.⁷ This system can be applied to the hydroarylation of alkynes in which addition of C–H bonds proceeds in an exclusive trans manner. *cis*-Hydroarylation of unactivated alkynes is promoted by rhodium catalysts such as Rh₄(CO)₁₂⁸ and RhCl(CO)(PMe₃)₂.^{9,10} However, these reactions require extreme conditions (220 °C, 25 kg/cm² pressure of carbon monoxide) or irradiation. During the course of our study on the reactivity of novel bimetallic complexes,¹¹ we found that dinuclear palladium complexes Pd₂R₂(μ-X)(μ-dpfam) [dpfam = *N,N'*-bis[2-(diphenylphosphino)phenyl]-formamidinate, R = *p*-Tol (**1a**), Me (**1b**)] catalyzed *cis*-hydroarylation of alkynes with unactivated arenes at lower temperatures in the presence of trialkylborane.



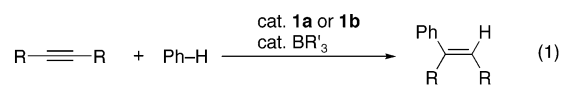
Pd₂R₂(μ-X)(μ-dpfam)
1a (X = OH, R = *p*-Tol)
1b (X = OH, R = Me)
1c (X = I, R = *p*-Tol)

Treatment of 3-hexyne (**2a**) with benzene in the presence of **1a** (2 mol %) and tri(*n*-butyl)borane (30 mol %) at 100 °C for 4 h afforded (*E*)-3-phenyl-3-hexene (**3a**) in 86% isolated yield (100% GC yield) (Table 1, entry 1). The *Z*-isomer of **3a** was not detected by ¹H NMR or GC. Although the dinuclear methylpalladium complex **1b** was also effective (entry 2), no product was obtained using the corresponding mononuclear methylpalladium complex PdMe(dpfa)¹¹ or the dinuclear complex [PdPh(PPh₃)(μ-OH)]₂,¹² without the binucleating ligand dpfam. Other typical palladium catalysts, such as Pd(OAc)₂ and Pd₂(dba)₃·CHCl₃, also were ineffective for the hydroarylation. Using triethylborane and triphenylborane as additives decreased the yield of **3a** remarkably (entries 4 and 5), and no reaction occurred in the absence of boranes. The hydrophenylation of several symmetrical internal alkynes (**2b–d**) proceeded under similar conditions, giving phenyl-substituted alkenes (**3b–d**) in satisfactory yields (entries 6–8). Although the reaction of 1-phenyl-1-butyne (**2e**) yielded both regioisomers, (*E*)-1,2-diphenyl-1-butene (**4**) and 1,1-diphenyl-1-butene (**5**), no other isomers were detected (entry 9 and eq 2). Treatment of (*Z*)-1,2-

Table 1. Pd-Catalyzed Hydrophenylation of Alkynes^a

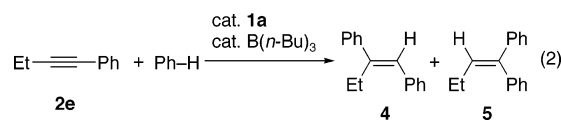
entry	alkyne	catalyst (mol %)	borane ^b	product	yield ^c (%)
1	2a	1a (2)	B(<i>n</i> -Bu) ₃	3a	100 (86) ^d
2	2a	1b (2)	B(<i>n</i> -Bu) ₃	3a	100
3	2a	1a (2)	B(<i>sec</i> -Bu) ₃	3a	100
4	2a	1a (2)	BET ₃	3a	31
5	2a	1a (2)	BPh ₃	3a	5
6 ^e	2b	1a (5)	B(<i>n</i> -Bu) ₃	3b	74 ^d
7 ^e	2c	1a (5)	B(<i>n</i> -Bu) ₃	3c	91 ^d
8 ^e	2d	1a (5)	B(<i>n</i> -Bu) ₃	3d	64 ^d
9 ^e	2e	1a (5)	B(<i>n</i> -Bu) ₃	4 + 5 (68:32)	73 ^d

^a A mixture of **2** (0.5 mmol), **1** (0.01–0.025 mmol), and borane (0.15 mmol) in benzene (2 mL) was heated at 100 °C for 4 h. ^b THF solutions. ^c GC yields based on alkynes. ^d Isolated yields based on alkynes. ^e Carried out at 120 °C for 17 h.



2a (R = Et)
2b (R = *n*-Pr)
2c (R = *n*-Bu)
2d (R = Ph)

3a (R = Et)
3b (R = *n*-Pr)
3c (R = *n*-Bu)
3d (R = Ph)



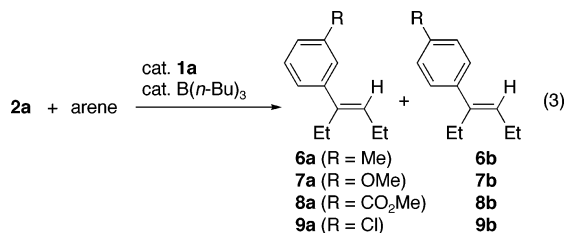
diphenyl-1-butene under the same reaction conditions did not afford **4**, indicating that *cis*-addition is kinetically favored. No product was obtained using terminal alkynes such as 1-octyne and ethynylbenzene.

Table 2. Pd-Catalyzed Hydroarylation of 3-Hexyne (**2a**) with Monosubstituted Benzenes^a

entry	arene	product	a:b ^b	yield ^c (%)
1	toluene	6a + 6b	73:27	64
2	anisole	7a + 7b	80:20	63
3	methyl benzoate	8a + 8b	61:39	71
4	chlorobenzene	9a + 9b	79:21	32 (75) ^d

^a A mixture of **2a** (0.5 mmol), arene (2 mL), **1a** (0.01 mmol), and B(*n*-Bu)₃ (0.15 mmol) was heated at 100 °C for 4 h. ^b Determined by GC. ^c Total GC yields based on **2a**. ^d The reaction was performed for 42 h in the presence of 5 mol % of **1a**.

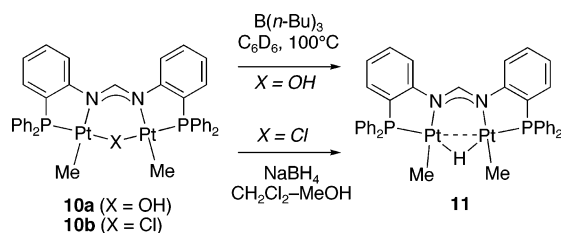
Table 2 summarizes results of hydroarylation of **2a** with several monosubstituted benzenes (eq 3). Both electron-rich and electron-poor arenes were reactive and afforded (*E*)-3-aryl-3-hexenes **6–9**, although the reaction of chlorobenzene required a higher catalyst loading and longer reaction time. The meta and para isomers were obtained in a ratio of ~2:1; no ortho isomer was detected from any of the reactions. This selectivity is similar to that observed in



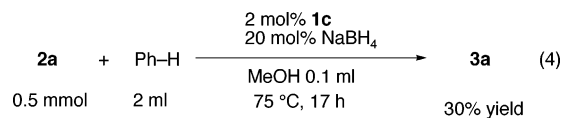
the iridium- and rhodium-catalyzed borylation of arenes¹³ rather than that of the Pd(OCOCF₃)₂-catalyzed *trans*-hydroarylation of alkynes via electrophilic C–H activation of arenes.⁷ No product was obtained using ortho-, meta-, and para-disubstituted benzenes.

Hydroarylation of **2a** in an equimolar mixture of toluene and anisole afforded **6** and **7** in nearly equal yields, 42% and 40%, respectively. In contrast, methyl benzoate was more reactive than toluene, yielding **8** and **6** in 64% and 28% yields, respectively, from the hydroarylation in their mixture. In a toluene/chlorobenzene mixture, reaction with toluene was suppressed relative to the reaction in neat toluene, giving **6** in 14% yield, although **9** was obtained in 32% yield, similar to that obtained in neat chlorobenzene. The preference for electron-poor arenes as well as the statistical product distributions is inconsistent with electrophilic C–H activation.⁷ The basis of these results cannot be understood until the mechanism for the hydroarylation is elucidated.

Scheme 1



To elucidate the role of boranes in the hydroarylation, complex **1a** or **1b** was treated with excess B(*n*-Bu)₃ at 100 °C in benzene. Despite the reaction of these complexes, no identifiable complex was obtained. In contrast, treatment of the corresponding dinuclear platinum complex **10a** with B(*n*-Bu)₃ afforded hydride-bridged complex **11** (Scheme 1). Similar hydride-bridged palladium complexes generated from **1a** or **1b** could not be isolated probably due to their instability.¹⁴ Because treatment of chloride-bridged complex **10b** with NaBH₄ also gave **11**,¹¹ this system was applied to palladium-catalyzed hydroarylation. Iodide-bridged complex **1c** did function as a catalyst for the hydroarylation in the presence of NaBH₄, giving **3a** in 30% yield (eq 4).



In summary, we have found dinuclear palladium complexes **1a–c** catalyzed *cis*-hydroarylation of alkyne with monosubstituted arenes, in which meta and para products were formed in statistical ratios. Further studies of reaction mechanisms and the improvement of catalyst activity are currently under investigation.

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Supporting Information Available: Experimental procedures and spectral data for all of the new compounds (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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