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Homocoupling reactions of terminal alkynes and arylboronic compounds catalyzed by in situ formed $Al(OH)_3$-supported palladium nanoparticles

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ABSTRACT

Palladium nanoparticles supported on newly generated $Al(OH)_3$ was found to be a highly efficient catalyst in oxidative homo-couplings of (Het)aryl alkynes, (Het)arylboronic acids and potassium (Het)aryltrifluoroborates, respectively. Moderate to excellent yields of symmetrical 1,3-diynes and biaryls were obtained under mild conditions.

1. Introduction

Considering the importance of environmental protection, it is very valuable and necessary to carry out chemical reactions under benign conditions using recyclable catalysts.[1] These catalysts are usually immobilized on a solid, and green support for easy separation and reuse.[2] Moreover, it has been demonstrated that support properties, which include the material itself and the structure, play an important role in the catalyst's performance and catalytic activities.[3] Therefore, the development of better catalyst supports is necessary to enhance the activity of the catalyst. On the other hand, nano-transition-metal catalyzed organic reactions have received much attention recently because of their extremely small size and large surface-to-volume ratio.[4] It is essential to choose suitable support materials with optimized structures to immobilize nanomaterial for specific chemical reactions.

1,3-Diyne derivatives are a prevalent and important class of intermediates with diverse applications in organic chemistry and functional materials, such as for the synthesis of natural products, pharmaceuticals, *p*-conjugated acetylenic polymers, and carbon-rich materials.[5] Transition-metal-catalyzed oxidative homocoupling of terminal alkynes provides an easy and efficient access to such compounds.[6] A number of catalyst systems have been explored for this reaction, including palladium,[7] nickel,[8] copper,[9] cobalt,[10] gold,[11] and silver.[12] Among them, the Pd-catalyzed Glaser-type coupling reactions represent one of the most promising methods for the synthesis of 1,3-diynes and have been broadly used to access 1,3-diynes.[13] Despite these advances, significant challenges still remain, owing to the difficulty of catalyst recovery. While the coupling with homogeneous catalyst can be accomplished with good results, efforts to develop efficient heterogeneous catalyst to facilitate the coupling have been met with relatively less success.[14] It is still necessary to develop highly efficient and environmentally friendly methods using nano-catalyst for the synthesis of broadly defined 1,3-diynes via a Glaser coupling pathway.

Given the prevalence of symmetric biaryls in medicinally relevant, natural, bioactive compounds and material sciences, it would be desirable to develop more highly efficient and greener methods using suitable compounds as partners via homo-coupling for the construction of such compounds. Although there have been several reports on the palladium-catalyzed homo-coupling of arylboronic acids,[15] the reports via nano-palladium-catalyzed approach are still rare.[16] Furthermore, palladium-catalyzed homo-coupling of potassium aryltrifluoroborates has been met with limited success.[17] Additionally, to the best of our knowledge, there is only one example that nano-palladium was utilized as a catalyst.[18]

Herein we report our efforts in nano-catalyst development (See Scheme 1) for such coupling reactions. With the $Al(OH)_3$-supported

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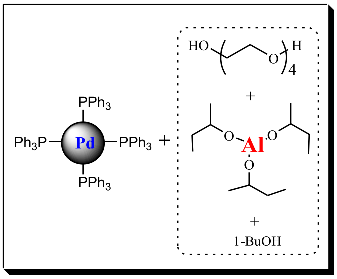


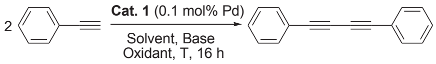
Scheme 1. Preparation of Pd nanoparticles catalyst **1**.

nano-Pd catalyst,[19] Glaser-type coupling can be realized with high yields and the homocoupling of potassium (Het)aryltrifluoroborates could smoothly be finished with modest to excellent yields. At the same time, we also describe the application of this catalyst in the homo-coupling of arylboronic acids.

2. Results and discussion

We commenced the optimization studies with phenylacetylene (**1a**) as a model substrate using different solvents and bases with a series of silver salts as oxidant in the presence of the nanoparticles Pd catalyst **1** (Table 1). First, a series of solvents, such as CH_3CN, toluene, DMSO, DMF, NMP, and Dioxane were screened. DMSO was proven to be the most effective solvent, while the others were not as effective (Table 1, entries 1–6). The investigation of bases revealed that 1 equiv of NaOAc exhibited superior results compared to NaOH, CsF, DIPEA, and KOAc (Table 1, entry 3 vs 7–10). Increasing the amount of the NaOAc (2 equiv) led to the lower yield (Table 1, entry 11). Next we studied the reaction by varying the reaction temperature. Unfortunately, the reaction was not significantly improved and the increasing reaction temperature to 90 °C led to 55% yield (Table 1, entries 12–14). Subsequently, our attention was focused on oxidants. Ag_2SO_4 was found to be the oxidant of choice giving the highest yield (Table 1, entry 20), whereas I_2, Ag_2O, $AgNO_3$, AgBr and $AgBF_4$ afforded the desired product in 48–71% yields (Table 1, entries 15–19). Excitedly, 99% yield was obtained when 30 mol % Ag_2SO_4 was adopted (Table 1, entry 22). Additionally, no reaction occurred in the absence of a palladium catalyst or in the presence of $Al(OH)_3$ served as a catalyst, and 44% and 58% yields were obtained when $Pd(Ph_3P)_4$ or $Pd/Al(OH)_3$ that was prepared by co-precipitation was utilized as a catalyst. These all indicated that this nano-Pd catalyst is essential for this reaction (Table 1, entries 23–26).

Table 1
Optimization for the palladium-catalyzed homo-coupling reaction of phenylacetylene[a]



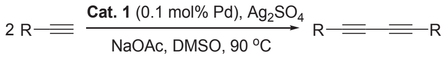
1a **2a**

Entry	Solvent	Base (equiv)	T (°C)	Oxidant (mol %)	Yield (%)[b]
1	CH_3CN	NaOAc (1)	50	—	3
2	Toluene	NaOAc (1)	50	—	Trace
3	DMSO	NaOAc (1)	50	—	39
4	DMF	NaOAc (1)	50	—	17
5	NMP	NaOAc (1)	50	—	11
6	Dioxane	NaOAc (1)	50	—	9
7	DMSO	NaOH (1)	50	—	Trace
8	DMSO	CsF (1)	50	—	14
9	DMSO	DIPEA (1)	50	—	29
10	DMSO	KOAc (1)	50	—	27
11	DMSO	NaOAc (2)	50	—	30
12	DMSO	NaOAc (1)	70	—	44
13	DMSO	NaOAc (1)	90	—	55
14	DMSO	NaOAc (1)	120	—	42
15	DMSO	NaOAc (1)	90	I_2 (10)	61
16	DMSO	NaOAc (1)	90	Ag_2O (10)	61
17	DMSO	NaOAc (1)	90	$AgNO_3$ (10)	48
18	DMSO	NaOAc (1)	90	AgBr (10)	54
19	DMSO	NaOAc (1)	90	$AgBF_4$ (10)	71
20	DMSO	NaOAc (1)	90	Ag_2SO_4 (10)	77
21	DMSO	NaOAc (1)	90	Ag_2SO_4 (20)	81
22	DMSO	NaOAc (1)	90	Ag_2SO_4 (30)	99
23[c]	DMSO	NaOAc (1)	90	Ag_2SO_4 (30)	Trace
24[d]	DMSO	NaOAc (1)	90	Ag_2SO_4 (30)	44
25[e]	DMSO	NaOAc (1)	90	Ag_2SO_4 (30)	Trace
26[f]	DMSO	NaOAc (1)	90	Ag_2SO_4 (30)	58

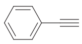
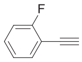
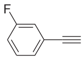
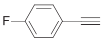
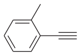
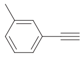
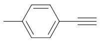
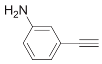
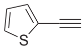
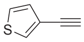
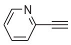
[a] Reaction conditions: **1a** (0.2 mmol), nano-Pd catalyst (0.1 mol % Pd), solvent (1 mL), time (16 h).
[b] Isolated yield.
[c] Without nano-Pd catalyst.
[d] 0.1 mol % $Pd(Ph_3P)_4$ was used as a catalyst.
[e] 0.1 mol % $Al(OH)_3$ served as a catalyst.
[f] 0.1 mol % $Pd/Al(OH)_3$ which was prepared by co-precipitation was utilized as a catalyst.

With the optimized reaction conditions in hand, we examined the scope of the functionalized phenylacetylene in order to establish the generality of the protocol. This transformation proved to be a general method for the preparation of various functional groups substituted symmetrical 1,3-diynes. Phenylacetylene with electron-donating or electron-withdrawing groups on aryl rings, such as methyl, amino, and fluoro all gave the corresponding symmetrical 1,3-diynes in good to excellent yields, thus implying that the electronic nature of the substrates has little influence on the yield (Table 2, entries 1–8). At the same time, the steric hindrance did not

Table 2
Nano-Pd catalyzed homocoupling of terminal alkynes[a]



1 **2**

Entry	Substrate	Time (h)	Product	Yield (%)[b]
1		16	**2a**	99
2		9	**2b**	97
3		9	**2c**	95
4		9	**2d**	99
5		12	**2e**	97
6		11	**2f**	99
7		8	**2g**	99
8		9	**2h**	85
9		16	**2i**	85
10		16	**2j**	86
11		48	**2k**	50

[a] Reaction conditions: **1** (0.2 mmol), nano-Pd (0.1 mol % Pd), NaOAc (0.2 mmol), DMSO (1 mL), Ag_2SO_4 (30 mol %), temperature (90 °C).
[b] Isolated yield.