

Palladium-catalyzed denitrogenative self-carbonylation of arylhydrazine using CO and O₂ as an ideal oxidant

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Abstract

An efficient Pd/Cu-catalyzed oxidative self-carbonylation of arylhydrazine with CO and molecular oxygen as an oxidant to afford symmetrical biaryl ketones via C-N bond activation has been developed. In this approach, arylhydrazine hydrochlorides are used as a green arylating agent which releases nitrogen and water as a byproduct. This developed protocol significantly restricts the for-mation of aryl iodide and homo-coupled azobenzene products even under favorable conditions. A library of symmetrical biaryl ke-tones with wide functionalities was synthesized in good yields under mild conditions.

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Palladium-catalyzed denitrogenative self-carbonylation of arylhydrazine using CO and O₂ as an ideal oxidant

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Comprehensive Summary

An efficient Pd/Cu-catalyzed oxidative self-carbonylation of arylhydrazine with CO and molecular oxygen as an oxidant to

Keywords

C(sp²)-N Bond activation 1 | Carbonylation 2 | Homogeneous catalyst 3 | Arylhydrazine 4 | symmetric biaryl Ketone 5

Background and Originality Content

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Transition metal-catalyzed carbonylative coupling reaction for the synthesis of polyfunctional biaryl ketones is attracted enormous attention because their core structural scaffolds are commonly embedded in various naturally occurring molecules,

Scheme 1. Pharmaceutical and biological significance of biaryl ketones

pharmaceuticals, and agrochemical industries.^[1] Some examples of naturally occurring biaryl ketones exhibit extraordinary antitumor activity **I**,^[2] photosensitizers **II**,^[3] electric material precursors **III**,^[4]

neoplastic agents **IV**,^[5] and anticancer activity **V** (Scheme 1).^[6] Given the significance of biaryl ketones, considerable effort has gone into their synthesis.

Conventionally, the biaryl ketone is synthesized using Friedel-Crafts acylation of arene of acid anhydrides or aryl halides with Lewis's acid. However, this method's use of the excess amount of Lewis acid causes problems with various functional groups, resulting in a large amount of waste and also suffering from regioselectivity.^[7] In this regard, the transition metal-catalyzed carbonylative cross-coupling reaction is a useful and simple technique for the synthesis of polyfunctionalized biaryl ketones. Generally, transition metal-catalyzed carbonylation reactions for the synthesis of biaryl ketones can be broadly classified into three groups: a) Synthesis of biaryl ketone via carbonylative cross-coupling reaction between organic halides and nucleophilic organometallic compounds.^[8] This approach commonly allowed the synthesis of both symmetric and unsymmetric biaryl ketones. b) palladium-catalyzed homo-coupled reductive carbonylation of aryl halide in the presence of reducing agents.^[9] c) carbonylative self-coupling reaction of nucleophilic organometallic compounds under oxidizing agents.^[10]

Over the past decades, various catalytic synthetic processes have been established for the synthesis of symmetric biaryl ketones. The transition metal-catalyzed aerobic oxidation of terminal olefins to form symmetric and unsymmetric carbonyl compounds. The oxidative self-coupling of aryl aldehydes via decarbonylation forms biaryl ketones and biaryls (Scheme 1a, 1b).^[11] Although these transformations make an important contribution to biaryl ketones synthesis, it suffers from the usage of moisture-sensitive ligands, harsh reaction conditions, limited substrate scope, and longer reaction time. Recently, several new synthetic approaches have been developed by chemists to reduce these types of problems. The transition metal-catalyzed carbonylative self-coupling reaction is the most effective approach for transforming different functionalized ketones.

Recently, Wu and co-workers reported Bismuth-mediated synthesis of symmetric biaryl ketone by oxidative carbonylation of triarylbismuths using m-CPBA (3-chloroperoxybenzoic acid) as an oxidant in chloroform under high CO pressure (40 bar) (Scheme 1c).^[12]

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Scheme 2. Transition metal-catalyzed synthesis of symmetric diaryl ketones. a) Aerobic oxidation of terminal alkenes; b) decarbonylative homocoupling; c, d, e) self-carbonylation strategies; f) a denitrogenative self-carbonylation strategy (*This work*).

The transition metal-catalyzed carbonylative self-coupling reactions with carbon monoxide (source of carbonyl) and aryl halides (aryllating agents) are able to synthesize symmetrical biaryl ketones, as other demonstrative paths have also been reported in the literature.^[13] More recently, Arndtsen developed an efficient strategy for palladium-catalyzed oxidative carbonylation of arenes using CO gas to synthesize biaryl ketones via C-H bond activation (Scheme 1d).^[14] On the other hand, the carbonylative self-coupling of organometallic nucleophiles (Ar-M) into symmetrical biaryl ketones is accomplished through transition metal catalysts under gaseous CO with the moisture-sensitive ligands (Scheme 1e).^[15]

Arylhydrazines have recently gained attention as prospective coupling partners because of their C-N bond stability, high dissociation energy, ease of availability, and high reactivity. In recent decades, arylhydrazines have developed as an efficient aryllating partner in a variety of C-C and C-X bond formation reactions.^[16] In 1857, Emil Fisher first synthesized phenyl hydrazine for the characterization of sugar molecules through

a hydrazone synthesis. The various numerous catalytic methods are also accessible for the preparation of these compounds, including the synthesis of various arylhydrazine derivatives through the diazotization of anilines and they could also be synthesized from aryl halides and hydrazine using transition metal (Pd, Cu) catalysts.^[17] Because of the environmental-friendly arylating source for the Pd-catalyzed coupling reactions with the releasing N₂ and H₂O as a by-product.

Our research group has been interested in emerging new carbonylation reactions via C-N bond activation for the last few years.^[18] Recently, we reported Palladium-catalyzed oxidative alkoxy carbonylation and aminocarbonylation of aryl hydrazine, aryl halides, and aryl boronic acids with alcohols and tertiary amines to synthesize the esters and tertiary amide derivatives via sp² and sp³ C-N bond activation.^[19] On the basis of these works, we focused on emerging an applicable and cost-efficient method for Pd-catalyzed denitrogenative self-carbonylation of arylhydrazines to afford the symmetrical biaryl ketones through C-N bond cleavage. Herein, we demonstrate the first-time Palladium-catalyzed oxidative carbonylation of aryl hydrazine hydrochlorides to form the series of symmetric biaryl ketones in moderate to good yields via C(sp²)-N bond activation under CO/O₂ with releasing N₂ and H₂O as a by-product.

Results and Discussion

We begin our study for the carbonylative self-coupling using phenylhydrazine hydrochloride **1a** as a model substrate to examine the effects of various optimized reaction conditions shown in Table 1.

Table 1. Optimization of Reaction conditions for carbonylative self-coupling of phenyl hydrazine^a

Entry	Catalyst	Base	[Cu]	Solvent	Time	Temp.	% Yield ^b	
							2a	3a
1	Pd/C	K ₂ CO ₃	—	Dioxane	12	100	05	—
2	Pd/C	K ₂ CO ₃	CuBr	Dioxane	12	100	25	—
3	Pd/C	K ₂ CO ₃	CuI	Dioxane	12	100	56	12
4	Pd/C	K ₂ CO ₃	Cu ₂ O	Dioxane	12	100	12	—
5	Pd/C	K ₂ CO ₃	Cu(OAc) ₂	Dioxane	12	100	17	—
6	Pd/C	K ₂ CO ₃	CuO	Dioxane	12	100	10	—
7	Pd(PPh ₃) ₄	K ₂ CO ₃	CuI	Dioxane	12	100	46	15
8	Pd (OAc) ₂	K ₂ CO ₃	CuI	Dioxane	12	100	49	16
9	PdCl ₂ (PPh ₃) ₂	K ₂ CO ₃	CuI	Dioxane	12	100	62	20
10	PdCl ₂	K ₂ CO ₃	CuI	Dioxane	12	100	59	18
11	PdCl ₂ (PPh ₃) ₂	K ₂ CO ₃	CuI	THF	12	100	45	09
12	PdCl ₂ (PPh ₃) ₂	K ₂ CO ₃	CuI	DMF	12	100	35	—
13	PdCl ₂ (PPh ₃) ₂	K ₂ CO ₃	CuI	DMSO	12	100	32	—
14	PdCl ₂ (PPh ₃) ₂	K ₂ CO ₃	CuI	MeCN	12	100	73	04
15	PdCl ₂ (PPh ₃) ₂	K ₂ CO ₃	CuI	Toluene	12	100	06	—
16	PdCl ₂ (PPh ₃) ₂	CS ₂ CO ₃	CuI	MeCN	12	100	07	—
17	PdCl ₂ (PPh ₃) ₂	Na ₂ CO ₃	CuI	MeCN	12	100	75	trace
18	PdCl ₂ (PPh ₃) ₂	Et ₃ N	CuI	MeCN	12	100	23	—
19	PdCl ₂ (PPh ₃) ₂	DBU	CuI	MeCN	12	100	04	—
20	PdCl ₂ (PPh ₃) ₂	Na ₂ CO ₃	CuI	MeCN	16	100	76	—
21	PdCl ₂ (PPh ₃) ₂	Na ₂ CO ₃	CuI	MeCN	08	100	67	—
22	PdCl ₂ (PPh ₃) ₂	Na ₂ CO ₃	CuI	MeCN	12	120	75	—
23	PdCl ₂ (PPh ₃) ₂	Na ₂ CO ₃	CuI	MeCN	12	80	69	—

^a **Reaction conditions:** Arylhydrazine hydrochloride (1.0 mmol), Catalyst (2 mol %), base (2 equiv.), co-catalyst (5 mol%), solvent (10 mL), 4 bar CO/O₂ with ratio (3:1), ^byield determined by GC-MS.

Initially, phenylhydrazine hydrochloride **1a** with 4 bar CO/O₂ with the ratio (3:1) was examined in 1,4

dioxane at 100 °C for 12 h in the presence of 5 mol% Pd/C and K₂CO₃ as a base, the targeted yield of benzophenone was obtained below 5%. Surprisingly, when CuBr was used as a co-catalyst, the yield of benzophenone was increased to 25% (Table 1, entry 2). Subsequently, we evaluate the various copper co-catalyst, among them CuI was the best and afforded a 56% yield of **2a** along with 12% of iodobenzene byproduct (Table 1, entry 3). Henceforth, CuI co-catalyst was used as a cocatalyst for further study of symmetric biaryl ketone synthesis. Notably, we found that the co-catalyst with molecular oxygen as an oxidant is important for this transformation. Next, we screened the various Palladium sources, and the homogeneous PdCl₂(PPh₃)₂ catalyst was found to be effective compared to the other catalysts (Table 1, entry 9). Then we studied the effects of solvents involves of 1,4 dioxane, THF, DMSO, acetonitrile, and toluene, among these solvents' acetonitrile is the more effective solvent and provides a good yield of **2a**, and byproduct **3a** was suppressed in this solvent (Table 2, entry 17). The impact of the base was then investigated using a variety of organic and inorganic bases, including Na₂CO₃, K₂CO₃, Cs₂CO₃, Et₃N, and DBU. Among these, Na₂CO₃ is the most effective for driving the C-N bond cleavage process. According to the time and temperature study, a reaction time of 12 hours and a temperature of 100 °C are necessary to achieve the highest yield of desired products (Table 1, entries 20-23).

With the optimal reaction conditions in hand (Table 1, entry 17), We began to explore the substrate scope of various substituted aryl hydrazine hydrochlorides. As concisely in Table 2, Gratifyingly, a series of aryl hydrazines hydrochlorides successfully underwent denitrogenative self-carbonylation reaction to synthesize symmetrical biaryl ketones.

Table 2. Carbonylative homo-coupling reactions of aryl hydrazines^a

Entry	Substrates	Products	Yield (%) ^[b]
1			75
2			67
3			70
4			71
5			57
6			48
7			61
8			60
9			55
10			64
11			67
12			61
13			63
14			65
15			60
16			52
17			46

^[a]**Reaction conditions:** Arylhydrazine hydrochloride (1.0 mmol), PdCl₂(PPh₃)₂ (2 mol %), Na₂CO₃ (2 equiv.), CuI (5.0 mol %), Acetonitrile (10 mL), 4 bar CO/O₂ with ratio (3:1),^[b] isolated yield.

Simple phenylhydrazine hydrochloride subjected to the oxidative carbonylation reaction affords a 75% yield of the benzophenone compound. A wide range of functional groups on phenyl hydrazine, such as electron-donating and electron-withdrawing groups are compatible. Generally, phenyl hydrazine with methyl substituents at *o*-, *m*-, and *p*-position to the phenyl ring underwent smooth carbonylation to form corresponding symmetric biaryl ketone product **2b**, **2c**, **2d** in moderate to good yield.

The phenyl rings bearing with di and tri substituted methyl groups could also work well to produce the corresponding desired products **2e** and **2f**. Moreover, the electron-rich arylhydrazine containing *m*-OMe,

and *p*-OMe are effectively worked, and the targeted biaryl ketone in yields of 61%, and 60% (**2g-2h**). The naphthalene-2-ylhydrazine hydrochloride, a poly aromatic could undergo carbonylative self-coupling to form symmetric polyaromatic ketone (**2i**) in 55% yield. Further, phenylhydrazine hydrochloride with electron-withdrawing substituents such as ortho, meta, and para (F, Cl, Br) could be afforded to corresponding biaryl ketones are **2j**, **2k**, **2l**, **2m**, **2n**, and **2o** with a yield of 64%, 67%, 61%, 63%, 65%, 60%, respectively. Notable, the carbonyl group-containing arylhydrazine moiety is also compatible with this optimal reaction condition to give **2p** in 52%, this methodology demonstrating that phenylhydrazine steric hindrance has little effect on the efficacy of the reaction. However, biologically active thiophen-3-ylhydrazine (**2q**) also performed well in the standard reaction condition, unfortunately, heteroaryl hydrazine are not worked well under the optimized condition. After evaluating the substrate scope for aryl hydrazine hydrochloride, we conduct a series of control experiments to acquire some insight into the reaction process. First, we accomplish the reaction in the absence of oxygen giving only 5% iodobenzene instead of homo-coupled biaryl ketone, and without CuI, no carbonylative homo-coupled product was noted. Furthermore, the reaction was performed in the absence of CO, we obtained selectively 92% yield of symmetric azobenzene. Notably, no biaryl ketone product was observed when the reaction was performed in the absence of base and Pd-catalyst. These results show that PdCl₂(PPh₃)₂, base, and CuI in the presence of molecular oxygen are essential for the reaction, as the lack of either fails to produce a homo-coupling biaryl ketone product.

Scheme 3. Control Experiments

A plausible reaction mechanism for denitrogenative self-carbonylation of aryl hydrazine hydrochloride is proposed according to the previous related literature work and the above experiments (Scheme 5).^[20] Initially, arylhydrazine hydrochloride **1** is converted into the simple arylhydrazine by sodium carbonate, and aryl palladium complex **A** is formed in situ through oxidative C-N bond activation of arylhydrazine with Pd(II) catalyst using Cu/O₂.^[21] Next, the insertion of CO to species **A** to form acylpalladium complex **B**. Subsequently, acyl palladium complex **B** reacts again with arylhydrazine **1** via C-N bond activation to generate complex **C**. Finally, reductive elimination of complex **C** to form symmetric coupling biaryl ketone **2a**, and regenerated Pd(0) species reoxidize to Pd(II) for the next cycle.^[21a]

Scheme 4. Plausible Reaction Mechanism

Conclusions

In summary, we have developed the first Palladium-catalyzed denitrogenative self-carbonylation of arylhydrazine hydrochloride with Cu/O₂ to afford symmetric biaryl ketones via C-N bond activation. The reaction performed well with PdCl₂(PPh₃)₂ as a catalyst with CO/O₂ and Na₂CO₃ as a base under mild reaction conditions. In this protocol the arylhydrazines are employed as a green arylating agent that released N₂ and H₂O as a byproduct. Additionally, this protocol provides a series of symmetric carbonylative ketones with a wide variety of functional group tolerance under CO/O₂ pressure.

Experimental

Materials and Methods:

All chemicals were procured from commercial providers and used without any purification technique. The reaction was studied by thin-layer chromatography (TLC) and GC-MS. The products were purified by column chromatography using a PET ether/EtOAc system. The ¹H and ¹³C NMR spectroscopic data of purified products were recorded on Agilent- 400 MHz (at 400, and 101 MHz respectively) spectrometer, The residual solvent signals such as (CHCl₃) and (CDCl₃) for ¹H and ¹³C NMR spectra. Coupling constant (J) values were expressed in Hz.

General Procedure for Synthesis of Symmetric Biaryl Ketones from Aryl hydrazine hydrochloride:

In a 100 mL reactor the mixture of aryl hydrazine hydrochloride (1 mmol), PdCl₂(PPh₃)₂ (2 mol%) and CuI (5 mol%) and Na₂CO₃ (2 equiv.), in acetonitrile (10 mL) were added and pressurized with 4 bar CO/O₂ in a ratio of (3/1). This reaction mixture was heated at 100 °C with constant stirring for 12 h. After the reaction, the reactor was cooled at room temperature, and remained gas was vented carefully. The reaction mixture was diluted with ethyl acetate (10 mL) and then washed with water. The organic layer fraction was dried over sodium sulphate and concentrated under rotary evaporation. Then obtained crude residue was monitored by GC-MS, and purified by column chromatography (pet ether: ethyl acetate, 80/20 v/v). The desired product was separated by chromatography and confirmed by GC-MS, and NMR techniques.

Supporting Information

The supporting information for this article is available on the WWW under <https://doi.org/10.1002/cjoc.2021xxxxx>.

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Entry for the Table of Contents

Palladium-catalyzed denitrogenative self-carbonylation of arylhydrazine using CO and O₂ as an ideal oxidant
 Pd/Cu-catalyzed denitrogenative self-carbonylation of arylhydrazine hydrochlorides to synthesize symmetrical biaryl ketone
