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Palladium-Catalyzed Aerobic Oxidative Cross-Coupling Reactions of Terminal Alkynes with Alkylzinc Reagents

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Over the past 40 years, transition-metal-catalyzed cross-coupling reactions have revolutionized chemical syntheses. This transformation, mainly involving R^1X as an electrophile and R^2M as a nucleophile, has maintained a robust momentum of development in all possible avenues, such as substrate scope, transmetalating reagents, catalysts, oxidants, etc. Recently, remarkable efforts to realize cross-coupling in an environmentally and economically benign manner have been made.[1−3] Oxidative coupling of R^1H with R^2M, which avoids the use of halides or halide equivalents, possesses practical advantages for applications and has attracted much attention.[4−9]

Challenges in this coupling manner still remain. One is that few examples of oxidative C(sp)−C(sp^3) bond formation have been reported, and extensive studies have mainly focused on the construction of C(sp^2)−C(sp^2),[5,10−33] C(sp^2)−C(sp^3),[34−39] C(sp^3)−C(sp^3),[36,40−42] and carbon−heteroatom[43−49] bonds. Another problem is related to the stoichiometric oxidants employed in this reaction. While typical terminal oxidants used in oxidative transformations include Cu, Ag, Mo, organic iodide, persulfate, and benzoquinone complexes, etc., direct utilization of the more practical molecular oxygen or air as oxidants remains a continuing challenge.[1−3,50,51]

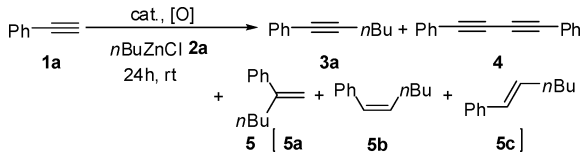
Recently, part of our research interest involves bond formation between two different nucleophiles (eq 1). Baran and DeMartino[52] investigated oxidative coupling between two different enolate anions, while Knochel and co-workers[53] reported copper-mediated oxidative coupling between alkynyllithium and arylmagnesium reagents; very recently, Cahiez and co-workers described oxidative cross-coupling between two different Grignard reagents[24] and organozinc reagents.[34] Using desyl chloride as the oxidant, we successfully developed oxidative cross-coupling reactions of organozinc reagents with organostannanes[54] and organoindium reagents.[55]

$$Nu^{1\ominus} + Nu^{2\ominus} \xrightarrow[\text{Oxidant}]{\text{Catalyst}} Nu^1\text{-}Nu^2 \qquad (1)$$

$$R^1{\equiv}H + R^2ZnX \xrightarrow[O_2]{\text{Catalyst}} R^1{\equiv}R^2 \qquad (2)$$

Oxygenation of Pd^0 could directly generate a $Pd^{II}(O_2)$ complex.[15,56−58] In addition, because of the weak acidity of C−H bonds of terminal alkynes, we envisioned that terminal alkynes could serve as nucleophiles in oxidative coupling reactions. Therefore, we decided to investigate the performance of terminal alkynes and alkylzinc reagents as two nucleophiles to undergo transmetalation with the Pd^{II} complex generated in the presence of O_2 and uncover new reactivities and selectivities under palladium-catalyzed aerobic conditions (eq 2). It is worth mentioning that for C(sp)−C(sp^3) bond-forming reactions by either oxidative coupling or tranditional coupling, very few examples have been reported in the literature.[59−61] Herein, we communicate our progress on the Pd-catalyzed aerobic oxidative cross-coupling between terminal alkynes and alkylzinc reagents using *air* as the oxidant.

Table 1. Palladium-Catalyzed Aerobic Oxidative Cross-Coupling Reactions of **1a** with **2a**[a]



entry	catalyst	equiv of **2a**	gas (v:v)	yield (%)[b] **3a**	**4**	**5**	**1a** (%)[c]
1	$Pd(OAc)_2$	3	air[d]	28	9	6	−
2	$Pd(OAc)_2$	3	CO/air (1:10)	57	7	10	−
3	$Pd(MeCN)_2Cl_2$	3	air[d]	30	8	6	−
4	$Pd(MeCN)_2Cl_2$	3	CO/air (1:10)	56	5	12	−
5	$Pd(PPh_3)_2Cl_2$	3	air[d]	9	49	5	−
6	$Pd(dba)_2$	3	air[d]	27	7	7	−
7	$Pd(dba)_2$	2	CO/air (1:10)	65	0	10	−
8	$Pd(dba)_2$	4	CO/air (1:10)	62	0	16	−
9	$Pd(dba)_2$	3	CO/air (1:1)	59	7	2	18
10	$Pd(dba)_2$	3	CO/air (1:5)	60	6	2	17
11	$Pd(dba)_2$	3	CO/air (1:10)	91	0	4	−
12	$Pd(dba)_2$	3	CO/air =1:20	82	0	6	−
13	$Pd(dba)_2$	3	Ar[e]	5	0	<1	79
14	$Pd(dba)_2$	3	O_2[f]	5	15	3	−

[a] Reaction conditions: All of the reactions were performed with **1a** (0.5 mmol), **2a**, Pd catalyst (5 mol %), and THF (2 mL) at room temperature for 24 h under the gas mixture at 1 atm pressure; CO and air were mixed by volume ratio. [b] Determined by GC. [c] Remaining **1a** determined by GC. [d] 1 atm air. [e] 1 atm Ar. [f] 1 atm O_2.

To investigate the Pd-catalyzed C(sp)−C(sp^3) oxidative coupling with O_2, phenylacetylene (**1a**) and *n*BuZnCl (**2a**) were selected as the typical coupling pair (Table 1). Under a dry air or oxygen atmosphere, almost all attempts led to polymerization of the alkyne, while **3a** was produced in low yields (entries 1, 3, 6, and 14). In comparison with other Pd complexes, $Pd(PPh_3)_2Cl_2$, which has a stronger electron-donor ligand, gave 9% target product along with 49% diyne and 5% alkenes (entry 5). Surprisingly, when carbon monoxide was mixed with the dry air in a 1:10 volume ratio at room temperature, the GC yield of C(sp)−C(sp^3) alkylation product was dramatically increased from 27% (entry 6) to 91% (entry 11) and exhibited satisfactory selectivity. When $Pd(OAc)_2$ was employed as the catalyst precursor, a 28% yield of the oxidative cross-coupling product **3a** was obtained (entry 1), while the yield improved to 57% (entry 2) in the presence of CO gas. The same phenomenon was observed using $Pd(MeCN)_2Cl_2$ as the catalyst precursor (entries 3 and 4). Varying the gas-volume ratio and the

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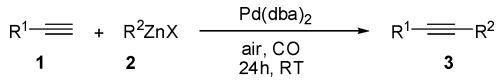
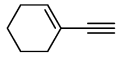
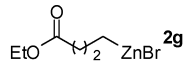
Table 2. Scope of Palladium-Catalyzed Aerobic Oxidative Cross-Coupling Reactions[a]



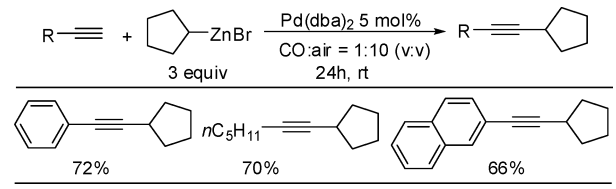
Entry	1	2	Yield[b] (%)
1[c]	R^1 = *m*-MeO-C_6H_4	MeZnCl **2b**	71
2[c]	R^1 = *p*-Ph-C_6H_4	**2b**	73
3[c]	R^1 = 1-Naphthyl	**2b**	84
4	R^1 = *o*-MeO-C_6H_4	*n*BuZnCl **2a**	86
5	R^1 = *m*-MeO-C_6H_4	**2a**	84
6	R^1 = *p*-MeO-C_6H_4	**2a**	81
7	R^1 = *p*-Cl-C_6H_4	**2a**	80
8	R^1 = *p*-Br-C_6H_4	**2a**	83
9	R^1 = *p*-Ph-C_6H_4	**2a**	77
10	R^1 = 1-Naphthyl	**2a**	80
11	R^1 = 2-Naphthyl	**2a**	76
12	R^1 = TES	**2a**	78
13		**2a**	75
14	R^1 = nC_5H_{11}	**2a**	82
15	R_1 = C_6H_5	nC_6H_{13}ZnCl **2c**	88
16	R^1 = 1-Naphthyl	**2c**	89
17	R^1 = nC_5H_{11}	**2c**	81
18	R^1 = *t*Bu	**2c**	74
19	R^1 = C_6H_5	nC_8H_{17}ZnBr **2d**	91
20	R^1 = nC_5H_{11}	**2d**	86
21	R^1 = *p*-Ph-C_6H_4	*i*BuZnBr **2e**	93
22	R^1 = 1-Naphthyl	**2e**	90
23	R^1 = C_6H_5	$PhCH_2CH_2ZnBr$ **2f**	79
24	R^1 = nC_5H_{11}	**2f**	75
25	R_1 = C_6H_5	 **2g**	93
26	R^1 = nC_5H_{11}	**2g**	85

[a] Reaction conditions: all of the reactions were carried out with **1** (0.5 mmol), organozinc reagent **2** (1.5 mmol), and $Pd(dba)_2$ (5 mol %) for 24 h under the gas mixture at 1 atm pressure. The CO/air volume ratio was 1:10, unless otherwise noted. [b] Isolated yields. [c] CO/air = 1:20 (v:v)

amount of organozinc reagent both resulted in lower yields of **3a** (entries 7−10 and 12).

Various terminal alkynes were then tested for this aerobic oxidative cross-coupling under the optimized conditions; the results are summarized in Table 2. In all cases, only trace amounts of carbonyl and dialkyl compounds were detected by GC−MS, and no diynes were found. When **2a** was employed, terminal alkynes with various substitutents such as aryl (entries 4−9), naphthyl (entries 10 and 11), olefin (entry 13), alkyl (entry 14), and triethylsilyl (TES) (entry 12) all gave the desired products with good to excellent isolated yields. In addition, both electron-withdrawing (Cl, Br) and electron-donating (OMe) substituents as well as ortho, meta, and para substitution showed little influence on this reaction (entries 4−8). When methylzinc chloride (**2e**), which has no β-H, was employed, reducing the CO/air volume ratio from 1:10 to 1:20 gave yields of 71−84% (entries 1−3). Relative to *n*BuZnCl, reactions using $(n\text{-}C_6H_{13})$ZnBr and $(n\text{-}C_8H_{17})$ZnBr gave slightly improved yields of 81−91% (entries 15−20), and the employment of *i*BuZnCl gave excellent yields (entries 21 and 22). Other organozinc reagents containing a functional group on R^2 were also well-tolerated, including phenyl (entries 23 and 24) and ester (entries 25 and 26).

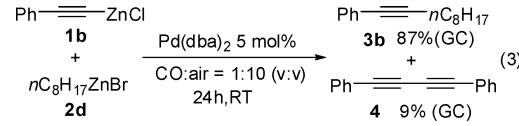
Table 3. Aerobic Oxidative Cross-Coupling Reactions of Alkynes with Cyclopentylzinc Bromide



When secondary alkylzinc reagents such as cyclopentylzinc bromide were employed as the nucleophile, the reactions could also produce the desired oxidative coupling products in 66−72% yield (Table 3).

From Table 1, it is clear that CO plays a critical role in terms of the chemical yield and selectivity. CO usually acts as a π-acidic ligand to coordinate with transition metals. Thus, we examined the role of dibenzylideneacetone (DBA), another well-known π-acidic ligand, in this reaction, and the same influence on both chemical yield and selectivity was observed (see the Supporting Information for details). As π-acidic ligands, DBA-type ligands are known to faciliate reductive elimination in transition-metal-mediated reactions.[62−64] Yamamoto and co-workers[65] have also demonstrated that CO at atmospheric pressure can act as a π-acidic ligand to induce reductive elimination. In this oxidative coupling reaction, we speculated that CO acts as a π-acidic ligand to promote the C(sp)−C(sp^3) reductive elimination.

To shed further light on the selectivity of this oxidative cross-coupling to form C(sp)−C(sp^3) bonds versus homocoupling to form C(sp)−C(sp) and C(sp^3)−C(sp^3) bonds, the reaction of alkynylzinc reagent **1b** and **2d** was investigated under the standard conditions (eq 3). Only 9% homocoupled diyne **4** was found by GC, and 87% cross-coupled product **3b** was obtained. This selectivity is fairly good but lower than in the reaction of **2d** with **1a** (**3b/4** = 98:2). Furthermore, the reaction of **1a** with **2d** was monitored via in situ FTIR (Figure 1A), and the kinetic behaviors of the homocouplings of **1b** and **2d** were also studied (Figure 1B,C, respectively). It is clear that the C(sp^3)−C(sp^3) homocoupling of **2d** is very slow. Only 2% hexadecane was determined by GC after 24 h. The global reaction rate for oxidative C(sp)−C(sp^3) cross-coupling was higher than that for C(sp)−C(sp) oxidative homocoupling.



Although different reaction rates for C(sp)−C(sp^3) and C(sp)−C(sp) coupling were observed, the excellent selectivity of the reaction of

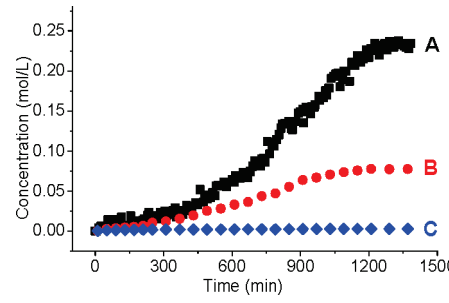


Figure 1. Kinetic profiles for (A) oxidative cross-coupling of **1a** with **2d**, (B) oxidative homocoupling of **1b**, and (C) oxidative homocoupling of **2d**. See the Supporting Information for details.

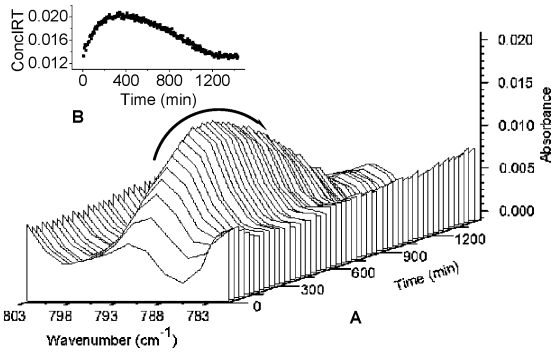


Figure 2. (A) 3D FTIR spectrum (803−780 cm^{-1}) for the reaction of **1a** with **2d**. (B) Kinetic profile (ConcIRT vs time) of the new component, which was assigned as the alkynylzinc reagent**2b**.

1a with **2b** (Table 1, entry 11; no diyne **4** was detected) cannot be rationalized. It is very interesting that from the 3D IR spectrum (Figure 2A), we noted an intermediate (typical absorbance at 790 cm^{-1}, which probably corresponds to in-plane aromatic ring bending) that not only increased slowly at first but also faded away. The kinetic profile of the intermediate concentration (ConcIRT) versus time (Figure 2B) clearly showed this transformation. By comparison with an authentic sample, we identified this intermediate as alkynylzinc reagent **1b**.

The cause for the excellent selectivity of this cross-coupling reaction of terminal alkynes with alkylzinc reagents can now be rationalized in terms of two factors: (1) a higher kinetic rate for C(sp)−C(sp^3) cross-coupling than for C(sp)−C(sp) homocoupling and (2) a low concentration of alkynylzinc reagents generated in situ from the reaction of alkylzinc reagents with terminal alkynes.

In conclusion, we have demonstrated an operationally simple and efficient method for the construction C(sp)−C(sp^3) bonds from terminal alkynes and alkylzinc reagents via Pd-catalyzed oxidative coupling. *Air* can serve as the sole oxidant in this oxidative coupling reaction, and CO was found to be critical in terms of enhancing the chemical yield and selectivity. Although DBA (DBA/Pd = 20: 1) also has a similar effect on the yield and selectivity, it is not desirable because it needs to be removed by column chromatography after the reaction. To the best of our knowledge, this is the first example of Pd-catalyzed aerobic oxidative C(sp)−C(sp^3) coupling employing terminal alkynes as one nucleophile and alkylzinc reagents as the other nucleophile. Further studies focused on extending the scope and gaining more detailed information on the exact mechanism are currently ongoing in this laboratory and will be reported in due course.

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Supporting Information Available: Experimental details and spectral data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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