

Cobalt-Catalyzed Oxidative Homocoupling of Arylzinc Species

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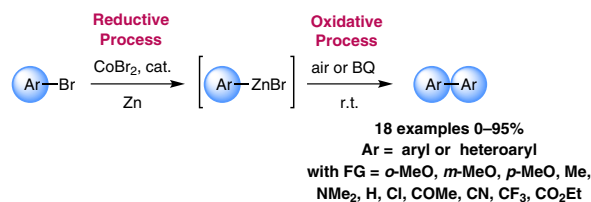
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Dedicated to the memory of Professor Jean F. Normant;
a brilliant scientist and a great person



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Abstract A novel procedure for the synthesis of functionalized symmetrical biaryl compounds is described. The reaction proceeds via the oxidative homocoupling of arylzinc species formed by cobalt catalysis in the presence of air or *p*-benzoquinone depending on the nature of the functional group.

Key words homocoupling, arylzinc, cobalt, symmetrical biaryl, oxidative coupling, air, *p*-benzoquinone

The biaryl motif plays a considerable role in various areas ranging from supramolecular chemistry to natural product synthesis.¹ Two classes of reactions allow their synthesis: homo- and cross-coupling. Historically, the Ullmann reaction was the first efficient process to form symmetrical biaryls through copper-promoted coupling.² Afterwards, due to the harsh conditions and stoichiometric amounts of copper required, new catalyzed processes were developed to synthesize symmetrical biaryls using catalysts such as palladium or nickel, starting from ArX (X = I, Br, Cl, OTf, OMe), and in the presence of a reducing agent.³ Following this approach, a few years ago, we reported a cobalt-catalyzed procedure for the reductive homocoupling of aryl halides.⁴ This efficient alternative involved simple and cheap CoBr₂ with Mn as a reducing agent and allowed the synthesis of various functionalized symmetrical biaryls. However, excess Mn was necessary and only low yields were obtained from aryl halides bearing electron-donating substituents.

The oxidative coupling of organometallic nucleophiles constitutes a complementary method for the construction of symmetrical biaryls. This other synthetic method implies an organometallic species in conjunction with an oxidant and a transition metal in most cases. Various organometal-

lic compounds can be used, such as silane, tin, boron, Grignard, lithium, manganese, and zinc derivatives with different catalysts.⁵ Although Rh was one of the first metals reported in this type of reaction, the homocoupling could be performed with other catalysts, such as the more common Pd and Ni.⁶ However, some of these catalysts have some disadvantages in terms of cost, toxicity, and the necessity for additional ligands. Nevertheless, new sustainable catalytic systems based on iron⁷ or cobalt⁸ have been developed and, more recently, a few reactions were reported without transition metals from aryl Grignard reagents, boronic acids, or diarylmanganese reagents using only an oxidant.^{5i,9} Although many common organometallic reagents (ArM; M = B, Sn, Si, Mn, and Mg) can react, arylzinc reagents are the best choice since they show high functional group compatibility compared to Grignard reagents and higher reactivity than organoboron, organotin, and organosilicon reagents. However, these arylzinc compounds should be prepared directly from aryl halides to be competitive with other organometallic reagents.

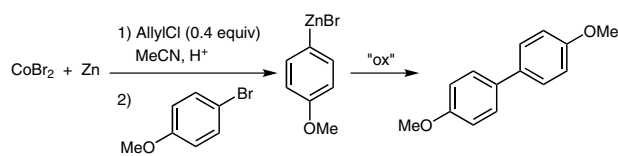
A few years ago, we established that cobalt catalysis allowed a simple and high-yielding preparation of a broad range of functionalized arylzinc species from readily available corresponding halides or sulfonates. These reactions require commercially available zinc dust along with acetonitrile as the solvent in the case of aryl bromides and iodides or with a mixture of acetonitrile/pyridine for aryl chlorides or triflates.¹⁰ Moreover, we have already demonstrated that cobalt salts used for the preparation of arylzinc derivatives can be also involved in the subsequent cross-coupling reaction.¹¹ Although considerable effort has been made, the development of other efficient routes to access symmetrical biaryls would be highly desirable. Thus, with the urgent demand for sustainable processes in the chemical industry, the development of new reactions involving cheap and less toxic catalysts as well as green and/or inex-

pensive oxidants has become an important research focus. Undoubtedly, using cheap cobalt salts as catalysts combined with a cheap oxidant for the synthesis of biaryls would be a valuable alternative.

Since we have cobalt in the medium, and the oxidative homocoupling of arylzinc species is somewhat described, the development of a useful and mild method for the construction of symmetrical biaryl backbones from arylzinc species under aerobic conditions will possibly provide a promising alternative. Herein, we report a versatile method for the dimerization of functionalized arylzinc species employing a simple cobalt salt as the catalyst associated with a simple oxidant. This simple dimerization proceeds smoothly with a variety of arylzinc species including various reactive groups such as esters, ketones, and nitriles.

We chose to start our study with an arylzinc species bearing an electron-donating group to access symmetrical biaryls. Therefore, we first investigated the oxidative coupling of the arylzinc compound from *p*-bromoanisole, generated via cobalt catalysis, in the presence of various oxidants. Actually, our previous co-catalyzed reductive homocoupling method gave low yields with this kind of compound. Various oxidants were tested at room temperature and the results are reported in Table 1.

Table 1 Cobalt-Catalyzed Homocoupling of *p*-MeOC₆H₄ZnBr with Various Oxidants^a



Entry	Oxidant	GC yield (%) of (MeOC ₆ H ₄) ₂ ^b
1	air	84
2	O ₂	82
3	BrCH ₂ CH ₂ Br	73
4	<i>N</i> -chlorosuccinimide	0 ^c
5	<i>p</i> -benzoquinone	79

^a All reactions were carried out using CoBr₂ (13 mol%), Zn (2.6 equiv), allyl chloride (40 mol%), TFA (trace), MeCN (5 mL) followed by addition of *p*-MeOC₆H₄Br (7.5 mmol). After consumption of the starting material, an oxidant (0.5 equiv) was then added.

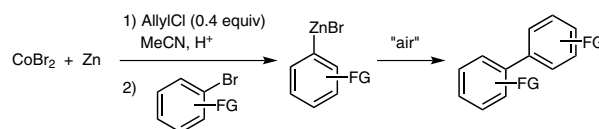
^b Based on *p*-MeOC₆H₄Br.

^c The corresponding ArCl was obtained in 54% GC yield.

All tested oxidants gave similar yields except *N*-chlorosuccinimide, which afforded the corresponding aryl chloride in 54% GC yield. Fortunately, the most environmentally friendly oxidant, air, gives the best result and yielded 84% of the homocoupling product. This green oxidant was used to dimerize a broad range of arylzinc bromides. Results are reported in Table 2. Good yields were obtained with a *para*-electron-donating group (Table 2, entries 1 and 3). Unfortunately, the yield decreased when this reaction was extend-

ed to an arylzinc species bearing an *ortho* substituent (Table 2, entry 2) or an electron-withdrawing group (Table 2, entries 5–8). With the latter, the corresponding phenols were observed in significant amounts. Interestingly, this method allowed the dimerization of the heterocyclic zinc species from 3-bromothiophene in moderate yield (Table 2, entry 9), whereas it was not possible with our previous cobalt-catalyzed reductive homocoupling.

Table 2 Cobalt-Catalyzed Homocoupling of Different ArZnBr with Air Oxidant^a



Entry	FG	GC yield (%) of ArZnBr	GC yield (%) of biaryl ^b	GC yield (%) of ArOH ^b
1	<i>p</i> -OMe	84	84	–
2	<i>o</i> -OMe	86	48	–
3	<i>p</i> -Me	80	80	–
4	H	81	59	–
5	<i>p</i> -MeCO	59	61	12
6	<i>p</i> -CN	81	39	44
7	<i>p</i> -CF ₃	80	58	20
8	<i>p</i> -CO ₂ Et	78	36	36
9	3-bromothiophene ^c	82	63	–

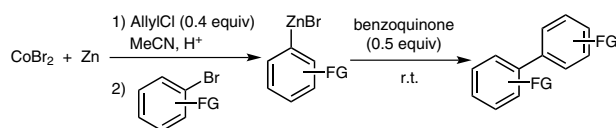
^a All reactions were carried out using CoBr₂ (13 mol%), Zn (2.6 equiv), allyl chloride (40 mol%), TFA (trace), MeCN (5 mL) followed by addition of aryl bromide (7.5 mmol). After consumption of the starting material, air was bubbled into the solution.

^b Based on aryl bromide.

^c Substrate.

To extend this method to aryl bromides bearing electron-withdrawing groups, a rapid screening of oxidants on various arylzinc species was performed: *p*-benzoquinone showed the largest scope. Consequently, we decided to perform the homocoupling reaction with various arylzinc species bearing either an electron-donating or an electron-withdrawing group with this oxidant (Table 3).

Generally, good to excellent yields were obtained with an electron-donating or an electron-withdrawing group in the *meta* or *para* position at room temperature. However, a moderate yield was obtained with a ketone on the aromatic cycle (Table 3, entry 8). As previously reported, a ketone might act as a strong chelating ligand for cobalt.¹² With a functional group in the *ortho* position, dimerization does not proceed correctly (Table 3, entries 2, 11, and 14), except in the case of *ortho*-acylated groups, which afforded moderate yields (Table 3, entries 9 and 16). In the same manner, the organozinc compound bearing a cyano group in the *ortho* position is very stable explaining the difficulty to ho-

Table 3 Cobalt-Catalyzed Homocoupling of Different ArZnBr with *p*-Benzoquinone as Oxidant^a

Entry	FG	GC yield (%) of ArZnX	Isolated yield (%) of biaryl ^b
1	<i>p</i> -OMe	87	71
2	<i>o</i> -OMe	90	4
3	<i>m</i> -OMe	93	77
4	<i>p</i> -Me	71	42
5	<i>p</i> -NMe ₂	62	59
6	H	74	75
7	<i>p</i> -Cl	89	95
8	<i>p</i> -COMe	64	45
9	<i>o</i> -COMe	0 ^c	28
10	<i>p</i> -CN	79	74
11	<i>o</i> -CN	97	6 ^d
12	<i>p</i> -CF ₃	82	79
13	<i>m</i> -CF ₃	85	60
14	<i>o</i> -CF ₃	91	0
15	<i>p</i> -CO ₂ Et	82	74
16	<i>o</i> -CO ₂ Et	73	48
17	3-bromothiophene ^e	88	79
18	2-bromothiophene ^e	71	52

^a All reactions were carried out using CoBr₂ (13 mol%), Zn (2.6 equiv), allyl chloride (40 mol%), TFA (trace), MeCN (5 mL) followed by addition of aryl bromide (7.5 mmol). After consumption of the starting material, *p*-benzoquinone (0.5 equiv) was then added.

^b Based on aryl bromide.

^c Only homocoupled product was obtained.

^d GC yield.

^e Substrate.

mocouple it (Table 3, entry 11). In the case of *ortho*-methoxy compounds, air seems to be more efficient (Table 3, entry 2 vs. Table 2, entry 2).

To get an explicit insight into the mechanism of this homocoupling reaction, we turned our attention towards the cobalt species involved. First, we have shown that the presence of cobalt is required in this oxidative dimerization of arylzinc species. The reaction of a commercial arylzinc compound carried out without cobalt, did not lead to the dimer even in the presence of an oxidant. As already reported, Co(0) is present at the end of the formation of the arylzinc.¹³ The cobalt species is oxidized by air or *p*-benzoquinone and reacts with the arylzinc by transmetalation to form the dimer after reductive elimination. We hypothesized that the active species was a Co(II) complex, that

could be then transmetalated with two arylzincs to form the dimer after reductive elimination. In order to check this hypothesis, we performed the oxidative dimerization of commercial arylzinc bromide in the presence of 0.5 equiv of CoBr₂ without any oxidant. The dimer was obtained in 73% yield, which is comparable to our method (Table 3, entry 6). The experiment was repeated but with a Co(I) source [0.5 equiv of CoCl(PPh₃)₃], only around 50% of ArZnBr was consumed even after 24 h. This result is not surprising, and could be explained by the disproportionation of Co(I) species into Co(0) and active Co(II).

In summary, we have developed a new cobalt-catalyzed homocoupling of arylzinc compounds, allowing the synthesis of various dimers. This reaction tolerates a large number of functional groups, and yields range from modest to excellent. The reactions involving electron-rich arylzinc bromides can be achieved using a green oxidant, air, while in other cases, *p*-benzoquinone is preferable. The low price of the catalyst and the mild and bench-friendly conditions make this homocoupling reaction an interesting alternative to other reductive or oxidative methods. However the steric hindrance of the arylzinc species has an influence on the outcome of the reaction. From a mechanistic point of view, some experimental evidence points towards the involvement of Co(II) in the dimerization by transmetalation.

All reactions were carried out in air unless otherwise stated. All glassware were oven-dried before use. All solvents and chemicals were obtained commercially and used as received unless otherwise mentioned. NMR spectra were recorded on a Bruker AC-300 SY spectrometer operating at 300.0 MHz for ¹H, 75.0 MHz for ¹³C, and 282.0 MHz for ¹⁹F and are internally referenced to residual solvents signals. IR spectra were recorded on a Perkin Elmer using the ATR method. UV/vis data were recorded in MeCN using a Cary 60 UV-Vis spectrophotometer. Mass spectra were obtained from the Ecole Polytechnique Mass Spectral facility. Gas-liquid chromatography (GLC) was performed on a Perichrom PR 2100 2317 Series gas chromatograph equipped with a split-mode, capillary injection system and flame ionization detectors using a SGE apolar ID-BP1 (25 m × 0.32 mm) column. Column chromatography was performed on silica gel with 60, 40–63 μm.

Oxidative Synthesis of Symmetrical Biaryl Using Air as Oxidant; General Procedure

To a solution of CoBr₂ (220 mg, 1 mmol, 13 mol%) and zinc powder (1.3 g, 20 mmol) in MeCN (5 mL) were successively added at r.t. allyl chloride (250 μL, 3 mmol) and TFA (50 μL), causing an immediate rise in temperature and color change to dark grey. After stirring the resulting mixture for 3 min, aryl bromide (7.5 mmol) was added. The medium was then stirred at r.t. until the aryl halide was consumed. The amount of the corresponding organozinc species was measured by reaction with I₂ and GC analysis using an internal reference (dodecane 100 μL). When the aromatic halide had been consumed, air was bubbled into the mixture. Then, when the organozinc had been consumed, the mixture was hydrolyzed by 2 M HCl and extracted with Et₂O. The organic layer was analyzed by GC.

Oxidative Synthesis of Symmetrical Biaryl Using *p*-Benzoquinone as Oxidant; General Procedure

To a solution of CoBr_2 (220 mg, 1 mmol, 13 mol%) and zinc powder (1.3 g, 20 mmol) in MeCN (5 mL) were successively added at r.t. allyl chloride (250 μL , 3 mmol) and TFA (50 μL), causing an immediate rise in temperature and color change to dark grey. After stirring the resulting mixture for 3 min, aryl bromide (7.5 mmol) was added. The medium was then stirred at r.t. until the aryl halide was consumed. The amount of the corresponding organozinc species was measured by reaction with I_2 and GC analysis using an internal reference (dodecane 100 μL). When the aromatic halide had been consumed, *p*-benzoquinone (405 mg, 3.75 mmol) was added and the mixture was stirred overnight. The mixture was hydrolyzed by 2 M HCl and extracted with Et_2O . The organic layer was dried (MgSO_4). Evaporation of solvent and purification by column chromatography (silica gel, petroleum ether/ Et_2O) afforded the symmetrical biaryl characterized by NMR (^1H , ^{13}C).

4,4'-Dimethoxybiphenyl

[CAS Reg. No.: 2132-80-1]

Yield: 570 mg (71%).

 ^1H NMR (300 MHz, CDCl_3): δ = 7.50 (d, J = 8.7 Hz, 4 H), 6.98 (d, J = 8.7 Hz, 4 H), 3.86 (s, 6 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 158.7, 133.5, 127.7, 114.2, 55.3.**2,2'-Dimethoxybiphenyl**

[CAS Reg. No.: 4877-93-4]

Yield: 32 mg (4%).

 ^1H NMR (300 MHz, CDCl_3): δ = 7.37 (ddd, J = 8.1, 7.5, 1.8 Hz, 2 H), 7.29 (dd, J = 7.4, 1.8 Hz, 2 H), 7.08–6.99 (m, 4 H), 3.81 (s, 6 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 157.1, 131.5, 128.7, 127.9, 120.4, 111.1, 55.7.**3,3'-Dimethoxybiphenyl**

[CAS Reg. No.: 6161-50-8]

Yield: 619 mg (77%).

 ^1H NMR (300 MHz, CDCl_3): δ = 7.44 (t, J = 79 Hz, 2 H), 7.32–7.21 (m, 4 H), 6.99 (dd, J = 8.2, 2.4 Hz, 2 H), 3.92 (s, 6 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 160.1, 142.7, 129.9, 119.8, 113.1, 112.9, 55.3.**4,4'-Dimethylbiphenyl**

[CAS Reg. No.: 613-33-2]

Yield: 287 mg (42%).

 ^1H NMR (300 MHz, CDCl_3): δ = 7.66 (d, J = 7.2 Hz, 4 H), 7.39 (d, J = 7.8 Hz, 4 H), 2.55 (s, 6 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 138.5, 136.8, 129.6, 127.0, 21.3.***N,N,N',N'*-Tetramethylbenzidine**

[CAS Reg. No.: 366-29-0]

Yield: 532 mg (59%).

 ^1H NMR (300 MHz, CDCl_3): δ = 7.47, (d, J = 8.8 Hz, 4 H), 6.82 (d, J = 8.8 Hz, 4 H), 2.98 (s, 12 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 149.0, 127.0, 113.3, 40.9; one quaternary carbon is not visible.**Biphenyl**

[CAS Reg. No.: 92-52-4]

Yield: 434 mg (75%).

 ^1H NMR (300 MHz, CDCl_3): δ = 7.84 (d, J = 7.5 Hz, 2 H), 7.66 (dd, J = 7.5, 7.3 Hz, 3 H), 7.58 (d, J = 7.3 Hz, 1 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 141.5, 129.0, 127.5, 127.4.**4,4'-Dichlorobiphenyl**

[CAS Reg. No.: 2050-68-2]

Yield: 795 mg (95%).

 ^1H NMR (300 MHz, CDCl_3): δ = 7.48 (d, J = 8.6 Hz, 4 H), 7.41 (d, J = 8.6 Hz, 4 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 138.4, 133.8, 129.1, 128.2.**4,4'-Diacetylbiphenyl**

[CAS Reg. No.: 787-69-9]

Yield: 402 mg (45%).

 ^1H NMR (300 MHz, CDCl_3): δ = 8.04 (d, J = 8.5 Hz, 4 H), 7.70 (d, J = 8.4 Hz, 4 H), 2.63 (s, 6 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 197.7, 144.3, 136.5, 129.0, 127.4, 26.7.**2,2'-Diacetylbiphenyl**

[CAS Reg. No.: 24017-95-6]

Yield: 250 mg (28%).

 ^1H NMR (300 MHz, CDCl_3): δ = 7.72 (dd, J = 7.1, 1.9 Hz, 2 H), 7.44 (quintd, J = 7.4, 1.5 Hz, 4 H), 7.15 (dd, J = 7.2, 1.5 Hz, 2 H), 2.24 (s, 6 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 201.6, 140.7, 138.7, 131.1, 130.8, 128.6, 127.6, 29.3.**4,4'-Biphenyldicarbonitrile**

[CAS Reg. No.: 1591-30-6]

Yield: 567 mg (74%).

 ^1H NMR (300 MHz, CDCl_3): δ = 7.78 (d, J = 8.3 Hz, 4 H), 7.69 (d, J = 8.3 Hz, 4 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 143.5, 132.9, 128.0, 118.5, 112.4.**4,4'-Bis(trifluoromethyl)biphenyl**

[CAS Reg. No.: 581-80-6]

Yield: 860 mg (79%).

 ^1H NMR (300 MHz, CDCl_3): δ = 7.77–7.69 (m, 8 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 143.2, 130.3 (q, J = 32.5 Hz), 127.6, 125.9 (q, J = 3.7 Hz), 122.4.**3,3'-Bis(trifluoromethyl)biphenyl**

[CAS Reg. No.: 580-82-5]

Yield: 653 mg (60%).

 ^1H NMR (300 MHz, CDCl_3): δ = 7.87–7.58 (m, 8 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 140.5, 131.5 (q, J = 32.3 Hz), 130.4, 129.5, 124.7 (q, J = 3.8 Hz), 123.9 (q, J = 3.8 Hz), 122.3.**Diethyl Biphenyl-4,4'-dicarboxylate**

[CAS Reg. No.: 47230-38-6]

Yield: 828 mg (74%).

^1H NMR (300 MHz, CDCl_3): δ = 8.07 (d, J = 8.2 Hz, 4 H), 7.60 (d, J = 8.3 Hz, 4 H), 4.35 (q, J = 7.1 Hz, 4 H), 1.37 (t, J = 7.1 Hz, 6 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 166.2, 144.1, 130.1, 129.9, 127.1, 61.0, 14.3.

Diethyl Biphenyl-2,2'-dicarboxylate

[CAS Reg. No.: 5807-65-8]

Yield: 537 mg (48%).

^1H NMR (300 MHz, CDCl_3): δ = 8.01 (dd, J = 7.7, 1.4 Hz, 2 H), 7.50 (ddd, J = 7.5, 7.5, 1.0 Hz, 2 H), 7.41 (ddd, J = 7.5, 7.5, 0.8 Hz, 2 H), 7.20 (dd, J = 7.5, 1.2 Hz, 2 H), 4.04 (q, J = 7.1 Hz, 4 H), 0.97 (t, J = 7.1 Hz, 6 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 167.1, 143.3, 131.3, 130.2, 129.9, 129.9, 127.1, 60.6, 13.7.

3,3'-Bithiophene

[CAS Reg. No.: 3172-56-3]

Yield: 493 mg (79%).

^1H NMR (300 MHz, CDCl_3): δ = 7.42–7.39 (m, 1 H), 7.37 (d, J = 1.8 Hz, 2 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 137.3, 126.4, 126.2, 119.9.

2,2'-Bithiophene

[CAS Reg. No.: 492-97-7]

Yield: 324 mg (52%).

^1H NMR (300 MHz, CDCl_3): δ = 7.30–7.19 (m, 2 H), 7.11–7.04 (m, 1 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 137.5, 127.9, 124.5, 123.9.

Supporting Information

Supporting information for this article is available online at <http://dx.doi.org/10.1055/s-0035-1562488>.

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