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# Cobalt-catalyzed reductive cross-coupling between benzyl chlorides and aryl halides

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**Abstract.** A new protocol for the direct reductive cobalt-catalyzed arylation of benzyl chlorides has been developed in order to form functionalized diarymethanes. A variety of reactive groups either on the aryl- or benzyl halides was employed. This represents the first cobalt-catalyzed reductive cross-coupling which does not require ligand and pyridine. A reaction pathway is proposed involving a radical benzyl species.

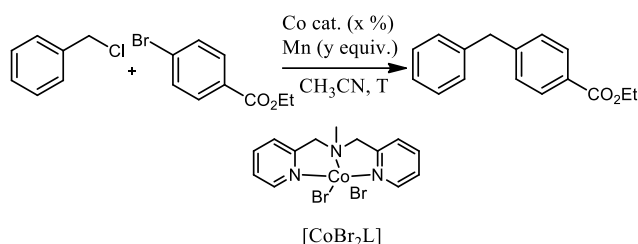
**Keywords:** cobalt; cross-coupling; diarymethanes; aryl halides; benzyl halides

Transition metal catalyzed cross-coupling reactions between organometallic nucleophile and organic electrophile have become the dominant approach to form C-C bonds during the last past decades.<sup>[1]</sup> For such transformations, palladium and nickel remain the most employed metals both in academia and industry,<sup>[2]</sup> nevertheless its high cost and scarcity or toxicity have motivated the search for alternatives. Then copper, iron, and cobalt which are more economical and/or eco-compatible were found efficient for a variety of coupling reactions.<sup>[3]</sup> A conceptually different approach consists in the direct cross-coupling of two electrophiles, which presents the advantage to avoid the handling and preparation of stoichiometric sensitive organometallic partner. Various combinations of aryl, alkenyl, acyl, allyl, or alkyl reagents were achieved with this methodology using Co, Pd, Ni, or Fe as metal catalyst and Zn, Mn, or Mg as reductant.<sup>[4]</sup> However very few reports deal with the preparation in such a way of the diarylmethane motif (*vide infra*), which is an important structural motif in pharmaceuticals.<sup>[5]</sup> This can be, nevertheless, conventionally prepared by electrophilic aromatic substitution (Friedel Craft benzylation)<sup>[6]</sup>, but this method is quite limited in term of scope and the regioselectivity may be difficult to control. Another possibility is an nucleophilic aromatic substitution on a benzyl derivative<sup>[7]</sup> which efficiency can be altered by steric hindrance. Aromatic

C-H activation offer another alternative way to access diarylmethanes.<sup>[8]</sup> However, the most employed strategy to prepare them remains transition metal catalyzed coupling reaction employing either electrophilic benzyl derivatives<sup>[9]</sup> or more rarely nucleophilic benzyl reagents<sup>[10]</sup> using Pd, Ni, Cu, Fe, or Co as catalyst. Lately, benzyl alcohol were also shown to be efficient as coupling partner in palladium-catalyzed Suzuki-Miyaura coupling.<sup>[11]</sup> Examples of direct electrophilic coupling to form diarylmethanes are rare: last year Weix et coll. elegantly demonstrated that benzyl mesylates reacted with arylhalides in presence of a nickel catalyst and a cobalt phthalocyanine co-catalyst assisting the formation of the alkyl radical.<sup>[12]</sup> Following our first report of direct reductive couplings of aryl bromide with alkyl halide<sup>[13]</sup>, using cobalt catalyst and manganese conducted in DMF in presence of pyridine, we were interested in developing milder reaction conditions for benzyl-aryl couplings. Therefore, we report here a cobalt-catalyzed easy synthesis of diarylmethanes by reductive cross-coupling of benzyl chlorides and aryl bromides tolerating various functional groups working at mild temperature, without ligand, with low equivalents of reductant, using acetonitrile as solvent, and no co-solvent.

In order to determine the optimal reaction conditions we focused on the reductive coupling of benzyl chloride and 4-bromo-ethylbenzoate with the objective to replace toxic DMF and suppress pyridine as co-solvent. To reach this goal, as we thought that a nitrogen-based ligand may help to stabilize the active catalytic species in the absence of pyridine, we tested beside CoBr<sub>2</sub> salt an unprecedented cobalt complex featuring an easy synthesized tridentate N<sub>3</sub> ligand (see SI for its synthesis and characterization). Results are gathered in table 1. The reactions were first conducted on 1 mmol scale of 4-bromo-ethylbenzoate (c~0.25 mmol mL<sup>-1</sup>) with 5% catalyst and 8 equivalents of manganese (entries 1-8). In those conditions higher temperatures did not change much the yields but

decrease the reaction time. In some cases, nevertheless the preformed complex  $[\text{CoBr}_2\text{L}]$  gave higher yields than cobalt salt (entries 1-2 and 5-6). Decreasing the quantity of manganese to 4 equivalents gave at 35°C 73 and 86% of the coupling product with  $\text{CoBr}_2$  and the preformed complex respectively. Reasoning that the lower yield obtained with the cobalt salt may be due to the purity of the commercial compound that on a small scale can have a strong influence on the efficiency, we then operate with a more concentrated reaction mixture (5 mmol of benzyl chloride in 4 mL acetonitrile). In those conditions at room temperature or 35°C, both catalysts were more or less as productive (entries 9-12). Decreasing once more the manganese loading to 2.2 equivalents (very close to the mechanistic limit of 2.05 equivalents, see scheme 2) did not dramatically influence the outcome of the reaction since the coupling product was formed in at least 70%. Interestingly with  $\text{CoBr}_2$  salt at room temperature 85% of product was observed. As these reaction conditions are very simple, we decided to explore the scope on this basis keeping in mind that both mild heating and use of a  $[\text{CoBr}_2\text{L}]$  may be attempted when those conditions are not satisfying.



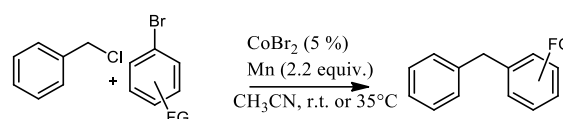
**Table 1.** Optimization study.<sup>[a]</sup>

	Co cat. (x %)	Mn y equiv	T (°C)	GC yield (%)
1 <sup>[b]</sup>	$\text{CoBr}_2$ (5%)	8	r.t.	72
2 <sup>[b]</sup>	$[\text{CoBr}_2\text{L}]$ (5%)	8	r.t.	88
3 <sup>[b]</sup>	$\text{CoBr}_2$ (5%)	8	35	85
4 <sup>[b]</sup>	$[\text{CoBr}_2\text{L}]$ (5%)	8	35	86
5 <sup>[b]</sup>	$\text{CoBr}_2$ (5%)	8	50	76
6 <sup>[b]</sup>	$[\text{CoBr}_2\text{L}]$ (5%)	8	50	84
7 <sup>[b]</sup>	$\text{CoBr}_2$ (5%)	4	35	73
8 <sup>[b]</sup>	$[\text{CoBr}_2\text{L}]$ (5%)	4	35	86
9 <sup>[c]</sup>	$[\text{CoBr}_2\text{L}]$ (5 %)	4	r.t.	84
10 <sup>[c]</sup>	$\text{CoBr}_2$ (5 %)	4	r.t.	82
11 <sup>[c]</sup>	$[\text{CoBr}_2\text{L}]$ (5 %)	4	35	82
12 <sup>[c]</sup>	$\text{CoBr}_2$ (5 %)	4	35	78
13 <sup>[c]</sup>	$[\text{CoBr}_2\text{L}]$ (5 %)	2.2	r.t.	75
<b>14<sup>[c]</sup></b>	<b><math>\text{CoBr}_2</math> (5 %)</b>	<b>2.2</b>	<b>r.t.</b>	<b>85<sup>[d]</sup></b>
15 <sup>[c]</sup>	$[\text{CoBr}_2\text{L}]$ (2 %)	2.2	35	78
16 <sup>[c]</sup>	$\text{CoBr}_2$ (2 %)	2.2	35	70

[a] aryl bromide and benzyl chloride were used in 1:1.5 ratio [b] Using 1 mmol of aryl bromide in  $\text{CH}_3\text{CN}$  (4 mL) [c] Using 5 mmol of aryl bromide in  $\text{CH}_3\text{CN}$  (4 mL). [d] 82% isolated yield.

First, we studied the influence of a functional substituent on the aryl halide (table 2). When the aryl bromide is substituted by an electron-withdrawing group (entries 1-11), the reaction worked quite well at room temperature (see for example entries 2-5, 8) except for the nitro derivative (entry 11) for which no reaction occurred as often observed in those types of cobalt-catalyzed reactions. Sometimes gentle heating of the reaction mixture to 35°C led to a slightly improved yield (entries 1, 7).

**Table 2.** Scope of aryl bromides.<sup>[a]</sup>



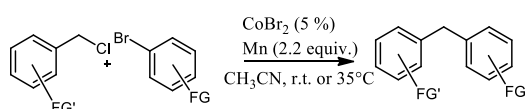
	ArBr (FG)	T (°C)	GC yield (%) at r.t./35°C	Yield (%) at r.t./35°C
1	(4-CN)	r.t./35	70/78	62/71
2	(2-CO <sub>2</sub> Et)	r.t.	80	74
3	(3-CO <sub>2</sub> Et)	r.t.	72	65
4	(2-CN)	r.t.	79	73
5	(4-CF <sub>3</sub> )	r.t.	78	71
6	(2-CF <sub>3</sub> )	r.t.	71	61
7	(3-CF <sub>3</sub> )	r.t.	61/72	50/64
8	(4-COMe)	r.t.	90	84
9	(2-COMe)	r.t./35	66/65	-/57
10	(4-SO <sub>2</sub> Me)	r.t.	88	85
11	(4-NO <sub>2</sub> )	r.t.	- <sup>[b]</sup>	-
12	(4-Cl)	r.t./35	65/74	58/69
13	(2-Cl)	r.t./35	66/72	58/67
14	(3-Cl)	r.t./35	72/75	65/-
15	(4-F)	r.t./35	60/57	54/-
16	(2-F)	r.t./35	58/56	52/-
17	(3-F)	r.t./35	68/71	65/-
18	(H)	35	70	<sup>[c]</sup>
19	(4-Me)	r.t.	72	<sup>[c]</sup>
20	2-napht	r.t./35	61/78	53/71
21	(4-SMe)	r.t./35	57/68	51/64
22	(4-OMe)	r.t./35	45/61	-/57
23	(4-NMe <sub>2</sub> )	35	60	51

[a] All reactions were carried out on 5 mmol of ArBr, 7.5 mmol of  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ , 11 mmol of Mn with 0.25 mmol of  $\text{CoBr}_2$  in  $\text{CH}_3\text{CN}$  (4 mL) with TFA (0.1 mL) [b] No reaction occurred [c] the coupling product can not be separated from the side ones.

This positive effect was not seen with the 2-COMe (entry 9). For chloro-substituted aryl bromides (entries 12-14), heating to 35°C made the reaction quicker and more effective with isolated yields around 65%. For

fluoro derivatives heating did not have this positive effect, the coupling product was isolated in 52, 65, 54% from 2-, 3-, 4-fluoro-benzene bromides respectively. Reaction with non-activated aryl bromides proceeded satisfactorily as well. Bromobenzene reacted with benzyl chloride at 35°C giving the coupling product in 70% GC yield, unfortunately the latter could not be chromatographically separated. The reaction with *p*-bromotoluene is comparable except it worked at room temperature. To couple 2-bromonaphthalene heating was also necessary allowing the coupling product to be isolated in 71% yield. Reactions are more difficult for deactivated aryl bromides (entries 21-23), for which isolated yield vary between 50 and 65%.

**Table 3.** Scope of benzyl chlorides.<sup>[a]</sup>

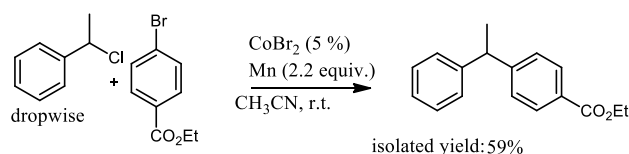


	(FG')	FG	T (°C)	GC yield at T°C	Yield (%) at T°C
1	(4-Me)	4-CO <sub>2</sub> Et	35	80	73
2	(3-Me)	4-CO <sub>2</sub> Et	35	84	76
3	(2-Me)	4-CO <sub>2</sub> Et	35	74	65
4	(3-OMe)	4-CO <sub>2</sub> Et	rt	68	64
5	(4-OMe)	4-CO <sub>2</sub> Et	r.t./35	32/28	-/-
6	(4-OMe)	4-CO <sub>2</sub> Et	r.t. <sup>[a]</sup> /r.t. <sup>[b]</sup>	63/38	58/-
7	(2-OMe)	4-CO <sub>2</sub> Et	r.t. <sup>[a]</sup>	60	54
8	(4-F)	4-CO <sub>2</sub> Et	r.t./35	52/76	-/70
9	(3-F)	4-CO <sub>2</sub> Et	35	58	55
10	(4-Cl)	4-CO <sub>2</sub> Et	35/35 <sup>[b]</sup>	20/72	66
11	(3-Cl)	4-CO <sub>2</sub> Et	35 <sup>[b]</sup>	73	68
12	(3-CF <sub>3</sub> )	4-CO <sub>2</sub> Et	35 <sup>[b]</sup>	68	63
13	(3-Me)	2-CN	35	84	76
14	(4-F)	4-CF <sub>3</sub>	35	62	- <sup>[c]</sup>

[a]: dropwise addition of benzyl chloride diluted in CH<sub>3</sub>CN (2 mL) at 1.5 mL h<sup>-1</sup>; [b] reaction with 4-iodo-ethylbenzoate in place of 4-bromo-ethylbenzoate; [c] the coupling product can not be separated from the side ones.

The scope of benzyl chlorides was then investigated (table 3). Methyl substituted benzyl chlorides coupled efficiently at 35°C (entries 1-3). These reaction conditions were efficient with 3-methoxybenzyl chloride giving 64% of coupling product but were inefficient when this electron-donating substituent was in position 2 or 4, since dimerization of benzyl chlorides occurred predominantly. To avoid this side reaction the benzyl chloride was added dropwise to the reaction mixture, which allowed to roughly double the GC yield (entry 6) giving the coupling product in 58 and 54% starting from 4-methoxy and 2-methoxy benzyl chloride respectively. Another strategy could be to increase the reactivity of the aryl halide using the

iodo derivative in place of the bromo, which may avoid dropwise addition (entry 6). However in that case the slow addition was more efficient. Nevertheless, the use of iodo-ethylbenzoate was an interesting alternative for chloro- and trifluoromethyl-substituted benzyl chlorides (see entries 10-12) whereas fluoro derivatives reacted satisfactorily at 35°C in non modified conditions (entries 8, 9). Couplings between a functionalized aryl bromide and a substituted benzyl chloride were also conducted (entries 13, 14) in decent yields

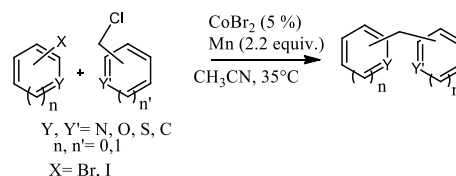


**Scheme 1.** Cross-coupling with  $\alpha$ -substituted benzyl.

This process was then investigated with a secondary benzylic chloride (scheme 1). As previously observed the  $\alpha$ -substitution considerably increased the reactivity of the benzyl chloride towards cobalt.<sup>[9f]</sup> Thus, dropwise addition of this compound allowed to obtain the cross-coupling product in good yield in a one step procedure.

This reductive coupling was also attempted with an heteroaryl ring either on the aryl or the alkyl partner, results are gathered in table 4. Reactions with 2-Br heteroaryl derivatives worked quite well except in the case of 2-Bromothiophene (entries 1, 3, 5). 3-Br thiophene coupled satisfactorily only with [CoBr<sub>2</sub>L] as precatalyst (entry 2) whereas for 3-Bromofuran, CoBr<sub>2</sub> was sufficient (entry 6). When the heterocycle was on the benzyl partner, reactions did not work in those simple conditions, indeed the dimerization of benzyl partner was generally the preferred pathway. This can be partially solved when using the corresponding aryl iodide (entry 7) together with the slow addition of the alkyl partner in the case of 3-benzylthiophene (entry 8).

**Table 4.** Coupling with heteroaromatic partner.<sup>[a]</sup>

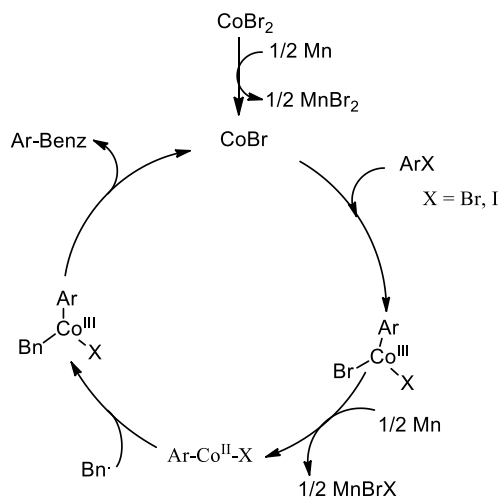


	ArX	ArCH <sub>2</sub> Cl	Yield Gc (isolated)
1	2-Br-Thiophene	BnCl	13/4 <sup>[b,c]</sup>
2	3-Br-Thiophene	BnCl	38/67 <sup>[b,c]</sup>
3	2-Br-pyridine	BnCl	99 (86)
4	3-Br-pyridine	BnCl	No reaction

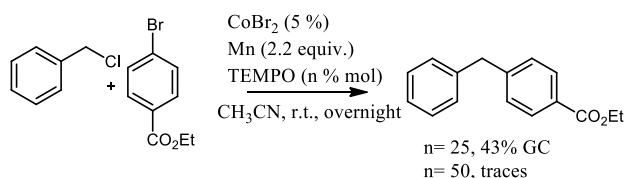
5	2-Br-furan	BnCl	70/59 <sup>[b,c]</sup>
6	3-Br-furan	BnCl	55/54 <sup>[b,c]</sup>
7	4-CO <sub>2</sub> Et-Ph-I	3-CH <sub>2</sub> Cl-thiophene	-/60 <sup>[d]</sup> (57)
8	4-CO <sub>2</sub> Et-Ph-I	2-CH <sub>2</sub> Cl-thiophene	20 <sup>[d]</sup> /36 <sup>[e]</sup>

[a] All reactions were carried out on 5 mmol of ArBr, 7.5 mmol of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Cl, 11 mmol of Mn with 0.25 mmol of CoBr<sub>2</sub> in CH<sub>3</sub>CN (4 mL) with TFA (0.1 mL) [b] with [CoBr<sub>2</sub>L] in place of CoBr<sub>2</sub> as precatalyst; [c] the coupling product can not be separated from the side ones. [d] reaction with 4-iodo-ethylbenzoate in place of 4-bromo-ethylbenzoate; [e] dropwise addition of benzyl chloride diluted in CH<sub>3</sub>CN (2 mL) at 1.5 mL h<sup>-1</sup> to 4-iodo-ethylbenzoate solution.

Our postulated mechanism (Scheme 2) is similar to the one we proposed for the aryl-alkyl,<sup>[13]</sup> aryl,<sup>[14]</sup> vinyl<sup>[15]</sup> coupling. To enter the catalytic cycle, the catalyst has to be reduced to Co<sup>I</sup>, then oxidative addition of aryl halide gives a Co<sup>III</sup> intermediate. The latter can be reduced by manganese to a Co<sup>II</sup> derivative, which is then able to react with the benzyl reagent yielding another Co<sup>III</sup> species, from which the coupling product is released by reductive elimination, regenerating the active catalyst. To prove the involvement of a benzyl radical, a control experiment was conducted in presence of TEMPO ((2,2,6,6-Tetramethylpiperidin-1-yl)oxyl). In that case the efficiency of the reaction was highly altered (scheme 3).



**Scheme 2.** Postulated catalytic cycle.



**Scheme 3.** Reaction with TEMPO.

In summary, we have reported a new practical Co-catalyzed cross-coupling of various functionalized benzyl chlorides and aryl halides allowing the synthesis of various diarylmethanes. This protocol tolerates a large number of functional groups and yields range from modest to excellent.

Remarkably, this procedure is the first reductive cross-coupling reaction without ligand and pyridine as co-solvent, and proceeds smoothly at room temperature or 35°C. Noteworthy when the catalyst loading was reduced to 2 mol% the preformed catalyst [CoBr<sub>2</sub>L] gave a better yield than CoBr<sub>2</sub>. The low price of the catalyst used and the mild and bench-friendly conditions make this reaction an alternative to more classical methodologies involving stoichiometric organometallic species. This new cobalt-catalyzed methodology allows easy access to functionalized diarylmethanes. The proposed mechanism suggests an intermediate radical benzylic species as already reported with alkyl compounds in the presence of cobalt catalyst.

## Experimental Section

To a solution of aryl bromide (5.0 mmol) and benzyl chloride (7.5 mmol) in CH<sub>3</sub>CN (4.0 mL) manganese powder (2.2 equiv., 11.0 mmol, 605 mg) was added. Trifluoroacetic acid (0.1 mL) was added to it in order to activate manganese followed by the addition of dodecane (0.1 mL) as internal standard. The reaction mixture was stirred for approximately 10 min. Then, CoBr<sub>2</sub> (5 mol%, 0.25 mmol, 55 mg) was added and the resulting reaction mixture was stirred at the indicated temperature until the disappearance of either of the starting materials. Upon completion, the mixture was then quenched with a solution of 2M HCl (25 mL) or with saturated NH<sub>4</sub>Cl solution (in case of amino compounds) and was stirred vigorously until layers turned clear. The solution was then extracted with CH<sub>2</sub>Cl<sub>2</sub> or EtOAc (3 x 25 mL), dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. Purification of the resulting oil or solid by flash chromatography over silica with pentane, petroleum ether/diethyl ether (or ethyl acetate) mixtures afforded the pure compounds.

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