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Direct Method for Carbon–Carbon Bond Formation: The Functional Group Tolerant Cobalt-Catalyzed Alkylation of Aryl Halides

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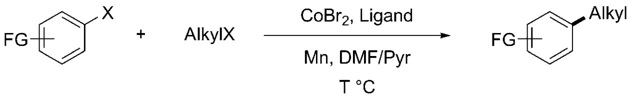
Dedicated to the memory of Professor Pascal Le Floch; an inspiring scientist and wonderful individual

Modern transition-metal-catalyzed reactions have been shown to be of indispensable value for organic synthesis.[1] In particular, the cross-coupling of alkyl halides, including problematic unactivated alkyl halides, have now emerged as promising candidates to complement and extend the scope of the traditional Friedel–Crafts alkylation.[2,3] The incorporation of a new alkyl chain on an aromatic moiety often proceeds by the metal-catalyzed coupling of stoichiometric organometallic derivatives (alkyl–M or aryl–M, M = Zn, B, Si, Sn, Mg, Mn, In, Al) using a large variety of transition metals, such as palladium, nickel, iron, cobalt, copper, rhodium, manganese, vanadium, or even silver.[2,4] However, it is intriguing to consider a direct approach for cross-coupling that does not rely on the utilization of preformed organometallic reagents, thus resulting in reduced step count and waste. Two main strategies have been reported, the palladium-catalyzed C−H activation for the domino *ortho*-alkylation/Heck coupling sequence,[5] and the direct cross-coupling of the corresponding halides.[6] The latter process involves a nickel-catalyzed activation of α-chlorocarbonyls for the synthesis of functionalized α-arylcarbonyl compounds. More recently, a magnesium-mediated direct cross-coupling using catalytic amounts of iron or cobalt salts has been developed by Jacobi von Wangelin and co-workers, thus documenting a practical alternative to the use of electrosynthesis or toxic nickel salts.[7] Despite the inherent practical advantages of these methods, the mechanistic fundament is the in situ formation of reactive Grignard reagents, which, in turn, narrows the substrate scope. The latter is generally restricted to electron-rich aryl and alkyl bromides and does not tolerate functional groups such as esters or ketones that are prone to react with organomagnesium reagents. We previously documented the development of straightforward procedures for the direct cobalt-catalyzed functionalization of aryl halides using $CoBr_2$/ligand/metal systems.[8] Employing non-toxic cobalt salts, we discovered highly reactive catalyst systems suitable for inexpensive and operationally trivial carbon–carbon bond-forming processes. Most importantly, these catalyst systems also showed compatibility with otherwise sensitive functionalized coupling partners. Herein, we report a versatile method for the direct functional group tolerant alkylation of aryl halides, a transformation that employs simple catalytic systems consisting of $CoBr_2$/Ligand/Mn. Our new cross-coupling protocol proceeds smoothly in the presence of phosphanes or bipyridines as ligands with a variety of alkyl halides, including challenging alkyl electrophiles bearing β-hydrogen atoms. Though the reaction requires presently activated aryl halides, the synthetic scope is in our view largely compensated by the use of a simple catalyst formed in situ from ubiquitous reagents and by the fact that sensitive functional groups such as esters, nitriles, or ketones are tolerated on both coupling partners, thus significantly extending the general scope of transition-metal-catalyzed alkylation of aryl halides (Scheme 1).



Scheme 1. General concept for the cobalt-catalyzed direct alkylation of aryl halides.

Having successfully developed methods using a $CoBr_2$/PPh_3/Mn system for the direct and selective synthesis of unsymmetrical biaryls,[8c] we directed our efforts to exploit such catalytic systems for the cobalt-promoted coupling of aryl and alkyl halides. We envisaged the use of readily avail-

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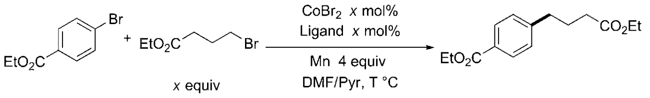
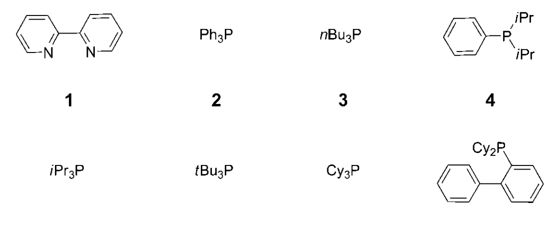
able yet poorly reactive alkyl bromides (as opposed to the corresponding iodides) bearing β-hydrogen atoms that would be subject to slow oxidative addition and subsequently to rapid β-hydride elimination hampering the coupling process.[2] Initial studies devoted to identifying suitable conditions were conducted using ethyl 4-bromobenzoate and ethyl 4-bromobutyrate as a model reaction (Table 1). The proposed alkylation was first examined at 65 °C in presence of 10 mol % $CoBr_2$ and 10 mol % 2,2′-bipyridine (**1**) in a mixture of DMF and pyridine using four equivalents of manganese and two equivalents of the alkyl bromide. Gratifyingly, the desired coupling product was obtained in 76 % yield (as determined by GC) within 4 h (Table 1, entry 1). Subsequent screening of ligand motifs unveiled promising effects of phosphane-type ligands on this reaction (Table 1, entries 3–7). Although initially employed bidentate nitrogen-based bipyridine **1** offered good activity, monodentate phosphane ligands, more precisely trialkyl phosphane **3** or dialkylaryl phosphane **4**, showed interesting reaction efficiency (Table 1, entries 5 and 6). We were pleased to find that the use of iPr$_2$PhP (**4**) afforded the corresponding product with an excellent GC yield of 99 % within 15 h (Table 1, entry 7). Moreover, the reaction temperature could be decreased to 30 °C and only a slight excess of alkyl bromide (1.1 equiv) was necessary to obtain a quantitative yield of the exclusively formed cross-coupling product. As highlighted in Table 1, presence of ligand was necessary (Table 1, entry 8) and related phosphanes led to inferior results in comparison to those obtained with ligand **4**.[9] Among the ligands that we have investigated, the mixed electronic properties of iPr$_2$PhP (Table 1, entry 7) compared favorably to Ph_3P or iPr$_3$P (Table 1, entries 9 and 11). Whereas iPr$_3$P was fairly effective, the use of less (nBu$_3$P, Table 1, entry 10) or more (tBu$_3$P, Cy_3P, Table 1, entries 12 and 13) sterically hindered trialkylphosphanes resulted in lower activities. Finally, Buchwald-type biaryl phosphane ligands **8**[10] gave moderate results under these conditions (Table 1, entry 14). Having successfully developed this protocol for the alkylation of aryl halides, we decided to undertake scope studies. The cobalt-catalyzed reactions of various aryl bromides with alkyl bromides containing electron-withdrawing groups were investigated (Table 2). Reactions of primary alkyl bromides gave the coupling products in good to excellent yields, and a range of sensitive functional groups were tolerated on both partners (ester, ketone, nitrile, trifluoromethyl Table 2, entries 1, 2, 4, 5, 8, and 11). Probably due to a cobalt chelation effect, 4-bromobenzonitrile and 4-bromobutyronitrile required higher catalyst loadings to afford good levels of efficiency in these reactions (Table 2, entries 4, 8, and 9). Electron-poor aryl bromides readily participated in a coupling with non-functionalized alkyl bromides in excellent yields (Table 2, entries 6, 7, 9, 10, and 12). Secondary alkyl bro-

Table 1. Ligand effect on cross-coupling between ethyl 4-bromobenzoate and ethyl 4-bromobutyrate.





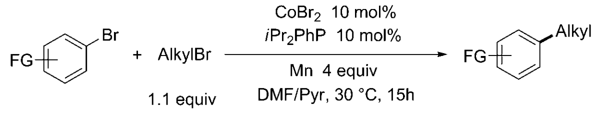
1 **2** **3** **4**

5 **6** **7** **8**

Entry	$CoBr_2$ [mol %]	Ligand [mol %]	RBr [equiv]	T [°C]	GC yield [%][a]	Time [h]
1	10	**1** (10)	2.0	65	76	4
2	20	**1** (20)	2.0	65	62	2
3	10	**2** (10)	2.0	65	50	2
4	20	**2** (20)	2.0	65	68	1
5	20	**3** (20)	2.0	65	72	1
6	20	**4** (20)	2.0	65	78	1
7	10	**4** (10)	1.1	30	99	15
8	10	none	1.1	30	63	24
9	10	**2** (10)	1.1	30	72	15
10	10	**3** (10)	1.1	30	55	15
11	10	**5** (10)	1.1	30	80	15
12	10	**6** (10)	1.1	30	74	36
13	10	**7** (10)	1.1	30	78	36
14	10	**8** (10)	1.1	30	63	72

[a] Full conversion of ethyl 4-bromobenzoate was observed. Yields determined by GLC analysis using an internal standard.

Table 2. Cobalt-catalyzed direct alkylation of aryl bromides with alkyl bromides: Substrate scope.



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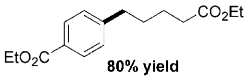
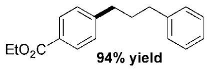
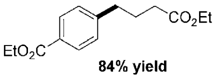
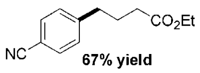
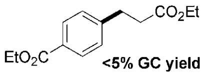
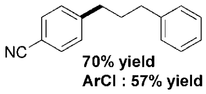
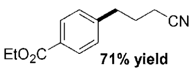
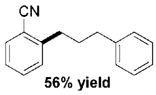
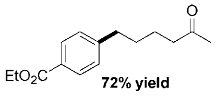
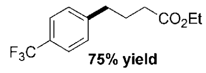
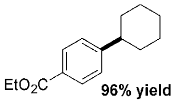
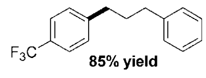
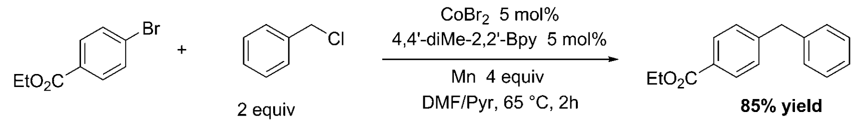
1		7	
2		8[a]	
3		9[a,b]	
4[a]		10	
5		11	
6		12	

[a] With 20 mol % $CoBr_2$/iPr$_2$PhP. [b] Reaction conducted with the corresponding aryl chloride at 65 °C with 20 mol % $CoBr_2$/iPr$_2$PhP and two equivalents alkyl bromide.

mides such as cyclohexyl bromide reacted efficiently with ethyl 4-bromobenzoate to afford the corresponding coupling product in 96 % yield (Table 2, entry 6). Satisfyingly, *ortho*-functionalized aryl bromide could also be employed to furnish moderate yields under the same conditions (Table 2, entry 10). Finally, preliminary results using aryl chlorides such as 4-chlorobenzonitrile showed the feasibility of this cobalt-catalyzed protocol to mediate a cross-coupling process with alkyl bromides under slightly modified conditions (Table 2, entry 9).

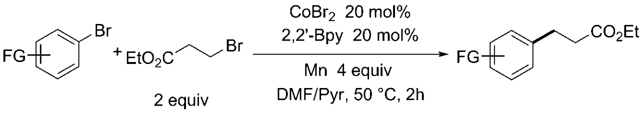
Unexpectedly, the cross-coupling of ethyl 3-bromopropionate remained unsuccessful under these conditions due to a rapid consumption of the alkyl partner by dimerization (as observed by GC) and presumably also by β-elimination and reduction (Table 2, entry 3).[11] The catalytic system involving *i*Pr_2PhP as a ligand remained inefficient even at higher temperatures (after 4 h with two equivalents of RBr at 50 °C, only a partial conversion of ArBr was observed at full conversion of alkyl bromide, 24 % GC yield).[12]



Scheme 2. Direct synthesis of diarylmethanes.

In contrast, the use of 2,2′-bipyridine allowed the reaction to go to completion and the desired coupling product was isolated in 76 % yield (Table 3, entry 1). Moreover, very low levels of conversion to the desired compound were accomplished by using pyridine only or PPh_3 (<5 % GC yield within a full conversion of ArBr).[12] Under these optimized conditions, the reaction proceeded smoothly with electron-poor aryl bromides. Moderate to good yields were obtained with *para*-functionalized aryl halides (Table 3, entries 1–3, 5, and 6). In this case, *ortho*-substitution appeared more problematic due to the high reactivity of the alkyl bromide coupling partner (Table 3, entry 4). However, slightly modified reaction conditions demonstrated that aryl chlorides could be employed as well affording the coupling products in reasonable to good yields (Table 3, entries 3 and 5).

Table 3. Cobalt-catalyzed direct cross-coupling of aryl bromides with ethyl 3-bromopropionate: Substrate scope.



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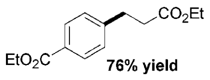
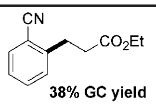
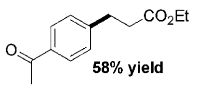
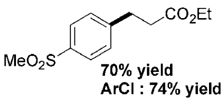
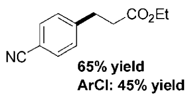
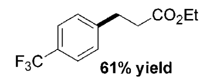
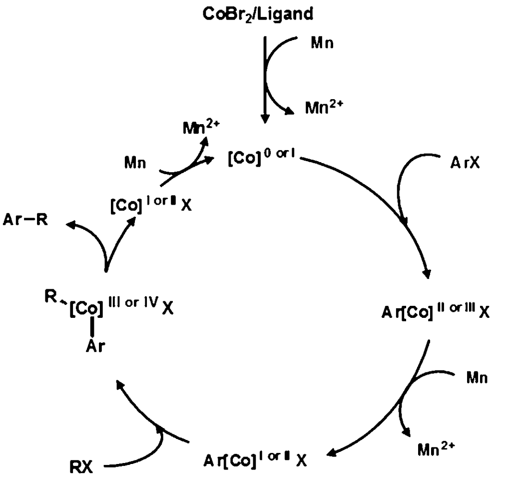
1		4	
2		5[a]	
3[a]		6	

[a] Reaction conducted with the corresponding aryl chloride at 65 °C and three equivalents of alkyl bromide.

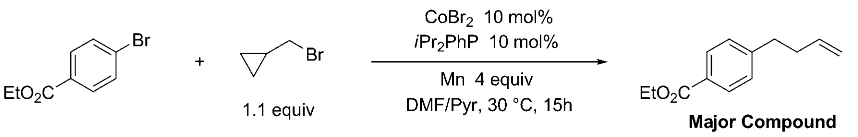
Lastly, we investigated the viability of a one-step synthesis of functionalized diarylmethanes that would constitute an interesting alternative to the Barbier-type procedure previously described by our group using $CoBr_2$ and zinc dust involving aryl zinc derivatives.[4i] As a representative example, the reaction of ethyl 4-bromobenzoate with benzyl chloride proceeded smoothly in the presence of 4,4′-dimethyl-2,2′-bipyridine to afford the desired diarylmethane in 85 % yield (Scheme 2). Under the same conditions, the use of the parent 2,2′-bipyridine allowed the formation of the corresponding diarylmethane in 74 % yield.[13]

Our current mechanistic hypothesis closely resembles our previous results describing the synthesis of biaryl compounds using cobalt complexes (Scheme 3).[8c,14] Initial reduction of a cobalt(II) complex should furnish a catalytically active low-valent cobalt species. Subsequent oxidative addition to the aryl halide gives an aryl cobalt intermediate that is, again, subject to reduction by the stoichiometric reductant (manganese). The key alkyl aryl cobalt complex formed upon a second, selective oxidative addition into the $C(sp^3)$–Br bond, is believed to display sufficient stability towards unproductive β-hydride elimination. Thus, reductive elimination can occur to furnish the cross-coupling product along with the regeneration of the catalytic active species. The generation of alkyl or aryl manganese derivatives as active



Scheme 3. Postulated mechanism for the direct alkylation of aryl halides.

species is unlikely since the reaction occurred with similar yields in the presence of air[15] or acetic anhydride.[16] However, a radical pathway based on single-electron transfer (SET) cannot be ruled out.[17,7b] As a preliminary result, under standard conditions, we found that reaction of ethyl 4-bromobenzoate with bromomethylcyclopropane afforded the corresponding product expected from a radical-based mechanism as the major compound with ArH (Scheme 4). Further studies are underway to further elucidate this mechanism.



Scheme 4. Reaction of ethyl 4-bromobenzoate with bromomethylcyclopropane.

In conclusion, we have demonstrated that a cobalt-based catalytic system is suited for the direct alkylation of functionalized aryl bromides and chlorides with unactivated or activated alkyl halides. $CoBr_2/iPr_2PhP/Mn$ has been shown to catalyze efficiently the direct Csp^2–Csp^3 coupling of various aryl bromides and even chlorides with relatively unreactive alkyl bromides bearing β-hydrogen atoms under mild conditions. A wide range of functionalized substrates containing ester, ketone, or nitrile moieties, as well primary or secondary alkyl bromides could be coupled in high yields. To the best of our knowledge, this method represents the first direct cross-coupling of aryl halides and alkyl bromides that is not limited to electron-rich substrates.[18] In the case of ethyl 3-bromopropionate or activated benzylic chlorides, a different choice of ligands facilitated comparably successful results. Further studies to extend the scope of this methodology and to gain detailed mechanistic insight are currently underway in our laboratory.

Experimental Section

Cross-coupling of aryl halides with alkyl bromides—general procedure: To a solution of $CoBr_2$ (10 mol %, 0.25 mmol, 55 mg) and manganese powder (4.0 equiv, 10 mmol, 550 mg) in a mixture of DMF (3 mL) and pyridine (0.5 mL) were successively added at room temperature the corresponding aryl bromide (2.5 mmol) and alkyl bromide (1.1 equiv, 2.75 mmol). Manganese powder was activated by traces of trifluoroacetic acid (50 μL) and the medium was then stirred at room temperature for 5 min until the smoke had disappeared. Then, iPr_2PhP (10 mol %, 0.25 mmol, 50 μL) was rapidly added and the medium was then stirred at 30 °C until aryl bromide was consumed (15 h). The amount of the corresponding coupling product was measured by GC using an internal standard (dodecane, 50 μL). The medium was filtered through a Celite pad and washed with ethyl acetate. The mixture was then poured into a solution of 2 N HCl or NH_4Cl (50 mL). The mixture was stirred vigorously until the layers turned clear. The solution was extracted with EtOAc (3 × 50 mL), washed with brine (1 × 100 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the resulting oil by flash chromatography over silica with petroleum ether/EtOAc mixtures afforded the title compounds.

Cross-coupling of aryl halides with ethyl-3-bromopropionate or benzyl chlorides—general procedure: To a solution of $CoBr_2$, 2,2′-bipyridine or 4,4′-diMe-2,2′-bipyridine, and manganese powder (4.0 equiv, 10 mmol, 550 mg) in a mixture of DMF and pyridine were successively added at room temperature the corresponding aryl bromide (2.5 mmol) and alkyl halide (2.0 equiv, 5.0 mmol). Manganese powder was activated by traces of trifluoroacetic acid (50 μL) and the medium was then stirred at 50 or 65 °C until aryl bromide was consumed (2 h). The amount of the corresponding coupling product was measured by GC using an internal standard (dodecane, 50 μL). The medium was filtered through a Celite pad and washed with ethyl acetate or Et_2O. The mixture was then poured into a solution of 2 N HCl or NH_4Cl (50 mL). The mixture was stirred vigorously until the layers turned clear. The solution was extracted with EtOAc or Et_2O (3 × 50 mL), washed with brine (1 × 100 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the resulting oil by flash chromatography over silica with petroleum ether/EtOAc or petroleum ether/Et_2O mixtures afforded the title compounds. See the Supporting Information for more details.

Acknowledgements

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Keywords: alkylation · cobalt · cross-coupling · homogeneous catalysis · synthetic methods

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