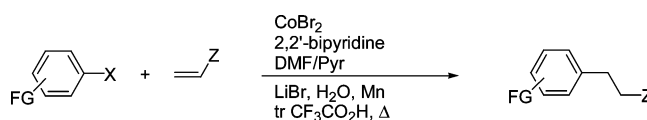# CoBr$_2$(Bpy): An Efficient Catalyst for the Direct Conjugate Addition of Aryl Halides or Triflates onto Activated Olefins

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FG = CO$_2$Et, CO$_2$Me, COMe, CN, SO$_2$Me, CF$_3$, H,
      OMe, NMe$_2$ (*ortho/ meta/ para*)
X = Cl, Br, OTf
Z = CO$_2$Et, CO$_2$Me, CN, CONMe$_2$...

An efficient cobalt-catalyzed method devoted to the direct conjugate addition of functionalized aryl compounds onto Michael acceptors is described. The CoBr$_2$(2,2′-bipyridine) complex appears to be an extremely suitable catalyst for the activation of a variety of aromatic reagents ranging from halides to triflates functionalized by reactive groups. This procedure allows for the synthesis of compounds resulting from 1,4-addition in good to excellent yields. The versatility of this original process represents a simple alternative to most known methods using organometallic reagents.

Introduction

The conjugate addition of organometallic reagents to electron-deficient olefins is a powerful method for the formation of new carbon−carbon bonds, yielding Michael adducts which represent useful synthons to further organic transformations.[1] In view of the paramount importance of this reaction in organic synthesis, new methods are continuously being developed to make this reaction more versatile and more reliable. The classical methods for the regioselective 1,4-addition of aryl halides generally involve a copper-catalyzed reaction[2] using air- and/or moisture-sensitive organometallic compounds such as aryllithium,[3] Grignard reagents,[4] arylmanganese,[5] and arylzinc.[6] Furthermore,

other transition-metal conjugate additions of main group organometallic reagents such as arylaluminum, -tin, -silicon, -titanium, -indium, and -boron compounds are reported under nickel,[7] palladium,[8] or rhodium catalysis.[9] In a previous work,

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SCHEME 1. General Procedure for the Cobalt-Catalyzed Conjugate Addition Process

FG = CO_2Et, CO_2Me, COMe, CN, SO_2Me, CF_3, H,
　OMe, NMe_2 (*ortho/ meta/ para*)
X = Cl, Br, OTf
Z = CO_2Et, CO_2Me, CN, $CONMe_2$...

SCHEME 2. Procedure for the Conjugate Addition of Ethyl *para*-Bromobenzoate onto Ethyl Acrylate

we have developed a new process for the addition of the electrochemically prepared arylzinc species onto activated olefins via a cobalt catalysis.[10] However, the main difficulty of these different methods is the preliminary preparation of organometallic reagents, especially when the aromatic nucleus bears a reactive group. Consequently, some chemical or electrochemical processes have been developed to avoid this step by direct activation of aryl halides. Homogeneous catalysis involving in situ reduction of transition-metal complexes remains of high interest.[11] For aryl halides, the catalyst precursor is generally a nickel complex, reduced either by an excess of zinc or electrochemically. In the first case, only a few examples of reactions utilizing aryl halides as coupling partners are reported and the majority of these are restricted to aryl iodides. Besides, direct electrochemical arylation of electron-deficient olefins performed with either nickel[12] or cobalt[13] catalysts in association with a sacrificial anode appears to be a suitable method for various aromatic halides.[14] Nevertheless, these electrochemical methods present some limitations. First, nickel is hazardous for environmental reasons. Second, in the cobalt-catalyzed reaction, $CoBr_2$ is only an efficient catalyst for the electrochemical addition of aryl bromides functionalized by electron-withdrawing groups onto methyl vinyl ketone. Moreover, all electrochemical reactions are generally considered as being more difficult to handle than conventional chemical methods. Given the importance of this reaction and the interest in cobalt-catalyzed reactions,[15] we have developed a new direct chemical procedure for the conjugate addition of different substituted aryl bromides, chlorides, and even triflates, bearing an electron-donating or -withdrawing group, on various activated olefins (Scheme 1).[16]

This one-step chemical procedure requires the use of $CoBr_2(2,2'-$ bipyridine) as the catalyst. The in situ generated low-valent cobalt species obtained by chemical reduction in the presence of the appropriate reducing metal activates aryl halides or triflates through this unprecedented procedure. The corresponding "aryl cobalt" species undergoes addition onto activated olefins to afford conjugate adducts. The use of manganese as a benign stoichiometric reducing agent in combination with an effective metal salt has already been originally described.[17]

This method avoids the prior preparation of organometallic reagents and exhibits high tolerance toward sensitive functional groups on the aromatic nucleus. Conjugate addition of a broad range of aromatic reagents can be obtained in a one-step reaction, under mild conditions, with quite short reaction times and furthermore onto various Michael acceptors such as α,β- unsaturated esters or nitriles. Herein, we wish to report the scope and limitations of this cobalt-catalyzed direct 1,4-addition of aromatic compounds.

Results and Discussion

Optimization of the Cobalt-Catalyzed Conjugate Addition. To optimize the reaction conditions, we have first investigated the reaction between ethyl *para*-bromobenzoate and ethyl acrylate modifying various parameters. The corresponding conjugate adduct is synthesized in the presence of 10 mol % of $CoBr_2(2,2'$-bipyridine), 1.1 equiv of ethyl acrylate, 1 equiv of H_2O, and 1 equiv of anhydrous lithium bromide in a mixture of DMF/pyridine at 50 °C. The reducing metal (Mn, 2 equiv) is activated by traces of trifluoroacetic acid (Scheme 2). The resulting amount of the coupling product is measured by GC using an internal standard (alkane) before isolation. Three byproducts such as the reduction product ArH, the homocoupling product Ar–Ar, and the unsaturated product of the Heck type could be observed in small amounts.

The presence of a lithium salt such as LiBr allows us to increase the reaction rate[2a,18] and the yields. With the use of 1 equiv of LiBr with respect to the aryl bromide, the conjugate adduct is obtained with a satisfactory isolated yield (80%). Concerning the nature of the salt, similar results are obtained with $FeBr_2$ or $MnBr_2$. When TMSCl is used as a reagent to "trap" the enolate anion generated and as an accelerating factor for 1,4-addition,[2a,19] it results, in our case, in a rapid conversion

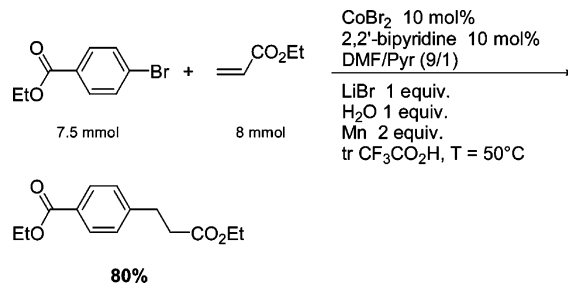(10) Gomes, P.; Gosmini, C.; Périchon, J. *Synlett* **2002**, 1673−1676.

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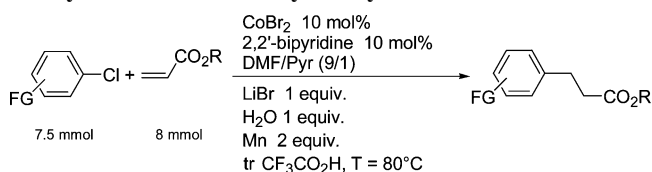
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SCHEME 3. General Procedure for the Conjugate Addition of Aryl Bromides onto Ethyl Acrylate

SCHEME 4. General Procedure for the Conjugate Addition of Aryl Chlorides onto Alkyle Acrylates
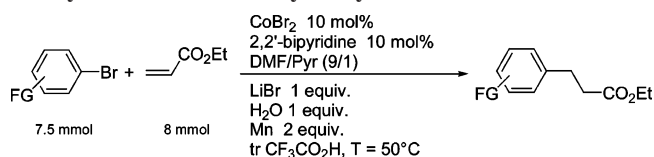
to the homocoupling product Ar−Ar. Then, for greater convenience, LiBr is used and its amount could be decreased to 0.5 equiv without any major modification. Besides, H_2O is essential in this process to prevent product evolution in the medium, mainly polymerization product. Consequently, $CoBr_2 \cdot xH_2O$ can be used instead of the anhydrous one. 2,2′-Bipyridine appears to be essential to stabilize the low-valent cobalt species in the medium. However, no important variations are noticed by increasing the ligand/cobalt ratio. Only 1 equiv of 2,2′-bipyridine vs $CoBr_2$ is required in this catalytic process. Moreover, the amount of cobalt complex affects the reaction rate but not the yields. Indeed, with 15 or 5 mol % of catalytic complex $CoBr_2$(2,2′-bipyridine), the efficiency of the reaction remains the same but reaction times are longer in the second case. Though Zn dust is able to reduce the cobalt complex instead of manganese, the nondesired corresponding reduction product (ArH) is detected in a greater amount to the detriment of the conjugate adduct, in the conditions described in Scheme 2. This may be rationalized by considering that Zn^{2+} ions released in the medium may form the arylzinc species[20] which evolves into ArH in the presence of water. This hypothesis is confirmed using both zinc dust and LiBr without H_2O. The amount of 1,4-adduct decreases (GC yield of 53%), and ArZnBr is a final product (ArZnBr in 23% yield). Concerning the amount of manganese dust, more than 1 equiv vs aryl bromide is sufficient to consume the starting material: no reaction is observed with the use of 1 equiv of manganese, and a GC yield of 57% was obtained with 1.5 equiv. Thus, 2 equiv of manganese has been found to deliver the optimum yield and a larger amount (≥ 2 equiv) has no effect. The manganese dust is activated by trifluoroacetic acid traces. Replacement of this Brönsted acid by iodine or acetic acid leads to poor results. Several other parameters such as the nature of the solvent and the presence of a cosolvent have been investigated. Because of the poor solubility of LiBr and 2,2′-bipyridine in acetonitrile/pyridine, such a mixture cannot be used. Though not necessary to affect the transformation, the use of pyridine as the cosolvent results in noticeable acceleration of the reaction, presumably through stabilization of the aryl cobalt species, as reported for the cobalt-catalyzed vinylation of aryl halides.[21] Using 1 or 2 equiv of ethyl acrylate affords the 1,4-adduct with quite similar GC yields. When the quantity of the α,β-unsaturated compound is increased, a secondary product, arising from a C-alkylation at the hypothetic enolate intermediate, is detected. The effect of temperature has also been examined. At room temperature, the yield is quite unchanged but the reaction time increases. On the other hand, at 80 °C, the coupling product ratio decreases and the main products formed are ArH and Ar−Ar.

Cobalt-Catalyzed 1,4-Addition and its Applications. We have thus extended this reaction to various functionalized aryl

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TABLE 1. Conjugate Additions of Aryl Bromides onto Ethyl Acrylate[a]

entry	FG	isolated yield (%)[b]	product no.
1	*p*-CO$_2$Et	80	**1**
2	*m*-CO$_2$Et	72	**2**
3	*p*-COMe	78	**3**
4	*m*-COMe	84	**4**
5	*p*-CN	70	**5**
6	*m*-CN	70	**6**
7	*p*-SO$_2$Me	83	**7**
8	*p*-CF$_3$	86	**8**
9	*m*-CF$_3$	83	**9**
10	*o*-CF$_3$	20	**10**
11	H	58	**11**
12	*p*-OMe	56	**12**
13	*m*-OMe	62	**13**
14	*o*-OMe	24[c]	**14**
15	*p*-NMe$_2$	46[c]	**15**

[a] Reaction conditions: 10 mol % of CoBr$_2$(2,2′-bipyridine), Mn, LiBr, H$_2$O, DMF/Pyr, 50 °C. [b] Conversion: 100%. [c] GC yields.

TABLE 2. Conjugate Additions of Aryl Chlorides onto Alkyl Acrylates[a]

entry	FG	R	isolated yield (%)[b]	product no.
1	*p*-CO$_2$Me	Me	64	**16**
2	*p*-COMe	Et	59	**3**
3	*p*-CN	Et	66	**5**
4	*m*-CN	Et	47	**6**
5	*p*-SO$_2$Me	Et	79	**7**
6	*p*-CF$_3$	Et	57	**8**

[a] Reaction conditions: 10 mol % of CoBr$_2$(2,2′-bipyridine), Mn, LiBr, H$_2$O, DMF/Pyr, 80 °C. [b] Conversion: 100%.

bromides and chlorides with alkyl acrylates under the conditions described in Schemes 3 and 4. Owing to the lower reactivity of the C−Cl bond, these halides require intramolecular activation by an electron-withdrawing group and their reactions need to be performed at 80 °C. However, increasing the temperature favors byproduct formation as reported previously. Results are reported in Tables 1 and 2.

Addition of aryl bromides bearing an electron-withdrawing group leads to excellent yields regardless of the position of the substituent (Table 1, entries 1−9). Yields decrease with electron-rich nuclei (Table 1, entries 12−15). Coupling in the ortho position remains difficult in these conditions (Table 1, entries 10 and 14). Work is still in progress to achieve the conjugate addition of ortho-functionalized aryl halides with electron-deficient olefins.

With aryl chlorides, yields are lower than those obtained with their bromide analogues and the proportion of byproducts such as ArH and Ar−Ar increases (Table 2, entries 2−6). However, the same reaction with *para*-chlorophenylmethyl sulfone yields the conjugate adduct with a 79% satisfactory yield (Table 2, entry 5).

The process described for aryl bromides has been extended to heteroaromatic bromides. Conjugate addition is efficient with
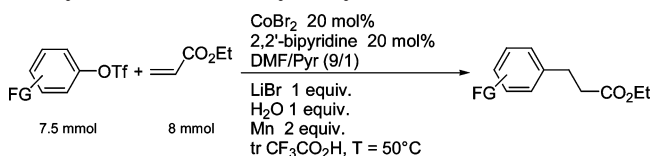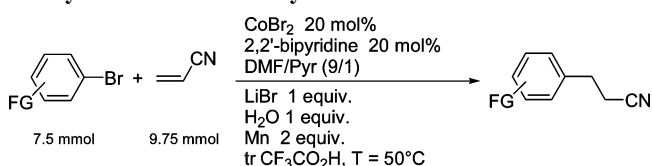
TABLE 3. Conjugate Additions of Aryl Triflates onto Ethyl Acrylate[a]

| entry | FG | isolated yield (%)[b] | | product no. |
		10 mol % of CoBr₂/Bpy	20 mol % of CoBr₂/Bpy	
1	H	69	82	**11**
2	*p*-CO₂Et	59	72	**1**
3	*p*-COMe	34	51	**3**
4	*p*-CN	31	69	**5**

[a] Reaction conditions: 10/20 mol % of CoBr₂(2,2′-bipyridine), Mn, LiBr, H₂O, DMF/Pyr, 50 °C. [b] Conversion: 100%.

SCHEME 5. General Procedure for the Conjugate Addition of Aryl Triflates onto Ethyl Acrylate

SCHEME 6. General Procedure for the Conjugate Addition of Aryl Bromides onto Acrylonitrile

TABLE 4. Conjugate Additions of Aryl Bromides onto Acrylonitrile[a]

entry	FG	isolated yield (%)[b]	product no.
1	*p*-CO₂Et	85	**19**
2	*m*-CO₂Et	73	**20**
3	*p*-COMe	82	**21**
4	*m*-COMe	63	**22**
5	*p*-CN	77	**23**
6	*m*-CN	71	**24**
7	*p*-SO₂Me	82	**25**
8	*p*-CF₃	79	**26**
9	*m*-CF₃	78	**27**

[a] Reaction conditions: 20 mol % of CoBr₂(2,2′-bipyridine), Mn, LiBr, H₂O, DMF/Pyr, 50 °C. [b] Conversion: 100%.

3-bromopyridine (68%, **17**) and gives a moderate yield with 3-bromothiophene (34%, **18**).

The reactivity of aryl triflates has also been investigated in the same conditions described in Scheme 3. In this case, aryl triflates appear less reactive than aryl bromides toward cobalt oxidative addition to form the aryl cobalt species (Table 3, column 3). Under these conditions, the reaction is too long and leads essentially to the formation of reduction product in the case of the carbonyl and nitrile groups. With these compounds, we have also noted a rapid deprotection of the triflate group giving the corresponding phenols. Surprisingly, the best results are observed with nonactivated aromatic triflate (Table 3, entry 1), whereas the corresponding aryl bromide does not perform as well (Table 1, entry 11). However, these yields can be improved by using more cobalt complex (Scheme 5; Table 3, column 4).

Encouraged by the good results obtained with ethyl acrylate, we have subsequently intended to extend this methodology to the conjugate addition of aryl bromides to acrylonitrile (Scheme 6). Table 4 displays the scope of this reaction upon using various

SCHEME 7. Mechanism Proposal for the Cobalt-Catalyzed Conjugate Addition of Aryl Species
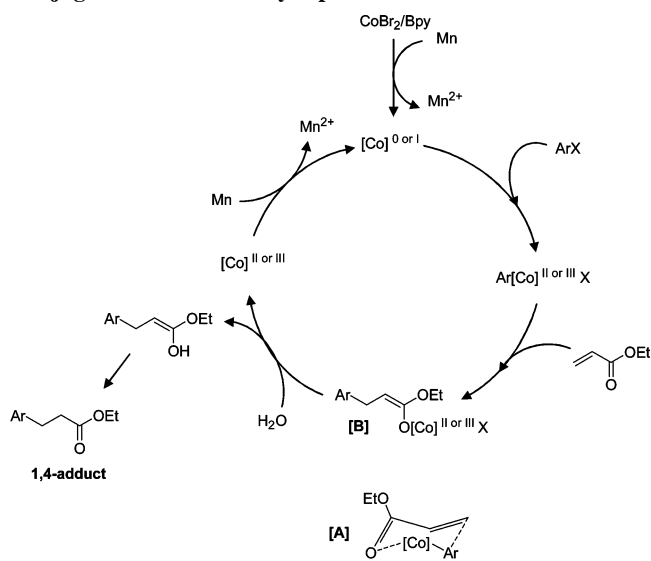
aryl bromides bearing electron-withdrawing groups and acrylonitrile.

Because of the lower reactivity of acrylonitrile, yields decreased compared to ethyl acrylate in standard conditions described in Scheme 3. However, 20 mol % of catalytic complex CoBr₂(2,2′-bipyridine) and a more important excess of acrylonitrile (1.3 equiv) are sufficient to perform the reaction with good yields. Results could be explained taking into account the tendency of acrylonitrile to polymerize in the medium.

Reactivity of other activated olefins has also been investigated. With *N,N*-dimethylacrylamide, the reaction is possible but its experimental conditions need to be optimized. Under standard conditions as described in Scheme 3, the conjugate adduct is obtained in low yield. However, 60% of the coupling adduct (**28**) is isolated using 3 equiv of *N,N*-dimethylacrylamide and ethyl *para*-bromobenzoate. We have attempted to extend this process to a more usual activated olefin such as methyl vinyl ketone according to Scheme 3. Unfortunately, the conjugate addition of ethyl *para*-bromobenzoate onto methyl vinyl ketone is not efficient at all and leads to a poor yield (24% GC yield) with a partial conversion under these standard conditions. This can be rationalized by considering that methyl vinyl ketone may act as a strong ligand for reduced cobalt in the medium. This important chelating effect may prevent reduced cobalt (Co^I or Co^0) from undergoing its oxidative addition at a sufficient rate.[22] Then, the use of 50% of cobalt complex leads to 50% (GC yield) of the coupling adduct with ethyl *para*-bromobenzoate. Works are still in progress to perform these reactions and decrease the amount of catalytic species.

Mechanistic Considerations. From a mechanistic point of view, as previously presented for the cobalt-catalyzed vinylation of aryl halides,[21,23] Co^II associated to 2,2′-bipyridine, and obviously pyridine, is reduced in a preliminary step by activated manganese to afford Co^I or Co^0 species in the medium. A radical pathway can be considered; however, the reaction in the

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presence of radical inhibitors (galvinoxyl free radical) affords similar results. The low-valent cobalt species most likely evolves with ArX by oxidative addition to form an aryl cobalt intermediate which could react via a nucleophile attack in a six-membered transition state [A] with the deficient electron olefin, leading to a cobalt enolate intermediate [B] (Scheme 7). The latter species reacts with residual water to give the expected 1,4-adduct releasing Co^{III} or Co^{II} species. These last species are regenerated into Co^{I} or Co^{0} thanks to the reducing agent.

Conclusion

We have developed a Co-catalyzed process devoted to the coupling of functionalized aryl compounds with activated olefins. This catalytic process uses a simple cobalt halide associated to 2,2′-bipyridine which appears to be an extremely suitable catalyst for a large variety of aromatic reagents ranging from halides to triflates functionalized by reactive groups. To our knowledge, this is the first efficient method for the direct 1,4-addition of functionalized aromatic compounds onto activated olefins without using stoichiometric organometallic reagents. The reaction affords good to excellent yields under simple and mild conditions. Work is now in progress both to elucidate the mechanism of this reaction and to extend it to other olefins.

Supporting Information Available: Experimental procedures and compound characterization data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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