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Cobalt-Catalyzed Vinylation of Aromatic Halides Using β-Halostyrene: Experimental and DFT Studies

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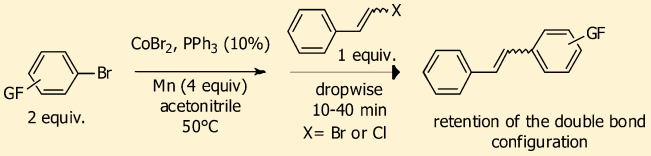
Supporting Information

ABSTRACT: A new protocol for the direct cobalt-catalyzed vinylation of aryl halides using β-halostyrene has been developed in order to form functionalized stilbenes. A variety of aromatic halides featuring different reactive group were employed. This method proceeded smoothly with a total retention of the double bond configuration in the presence of triphenylphosphine as ligand. Preliminary DFT calculations rationnalize these results and proposed a reaction pathway in agreement with the experimental conditions. This procedure offers a new route to the stereoselective synthesis of stilbenes.



INTRODUCTION

Stilbenes are natural compounds ubiquitous in plants.[1] Many compounds such as resveratrol[2] and combretastatin A-4[3] have been isolated and are used for their antitumoral,[4] anti-inflammatory,[5] neuroprotectiv,e[6] and cardioprotective[7] properties. Moreover, structure−activity studies have shown that the configuration (*Z* or *E*) of the compound is essential for their properties.[8]

Many studies deal with the synthesis of these compounds, forming either the double bond or one of the two corresponding single bonds. The double bond was formed by retro [2 + 2] cycloaddition such as Wittig,[9] Peterson,[10] or Julia[11] reactions or from an acetylenic compound by heterogeneous[12] or homogeneous[13] reduction or hydro/carbometalation[14] or by metathesis reactions.[15] One of the single bond can result from a Mizoroki−Heck reaction[16] or a metal-catalyzed cross-coupling reaction. These last reactions have been extensively studied with palladium- or nickel-based catalysts,[17] involving a vinyl halide and an aryl metal compound[18] or conversely an aryl halide and a vinyl metal compound.[19] Some other catalysts were used with success: rhodium,[20] iron,[21] manganese,[22] and cobalt[23] especially. All of the reactions described above deal with the synthetic difficulties associated with the preparation of the organometallic reagent especially when its organic precursor bears a reactive group. Therefore, to avoid this step, some direct cross-coupling reactions were developed by electrochemical or chemical processes to form stilbenes, but to the best of our knowledge, this domain remains under investigated.

Our team has already encountered some successes in direct cobalt-catalyzed reactions.[24] This cheap and nontoxic metal allowed us to form organometallic species[25] and many kinds of carbon−carbon bonds[26] in a simple manner. Among them, we have already performed double bond formations using cobalt-based catalysts such as the Heck reaction[27] and the vinylation of aromatic halides by electrochemical[28] and chemical[29] ways using vinyl acetates.

Herein, we report a new Co(II)-mediated cross-coupling reaction devoted to the generalization of these reactions to the direct vinylation of aromatic halides using the very reactive β-bromostyrene. The control of its reactivity and the retention of the double bond configuration are important problems that were addressed. Moreover, a mechanism is proposed for this new cobalt-catalyzed reaction based on the experimental results and DFT calculations.

RESULTS AND DISCUSSION

Experimental Studies. Having successfully developed methods using $CoBr_2/PPh_3/Mn$ system for the direct and selective synthesis of unsymmetrical biaryls, we first investigated these initial optimized conditions.[30] This preliminary study involving this system in a mixture of DMF/pyridine at 50 °C was highly encouraging (57% GC yield) with 2 equiv of β-bromostyrene and 1 equiv of phenyl iodide. We then optimized the reaction conditions: modification of the solvent, addition of cosolvents such as pyridine, change of the ligand, and the temperature.

According to all our previous studies, the reaction carried out in toluene or THF did not work: the reagents were recovered. The best results were obtained in the presence of $[CoBr_2(PPh_3)]$ as catalyst, using acetonitrile in place of DMF without any pyridine, leading to a 75% isolated yield (Scheme 1).

No improvement was observed in the absence of ligand or in the presence of 2,2′-bipyridine instead of PPh_3. Some other parameters such as the nature and amount of the reductant and the relative amounts of reagents were modified but without any improvement. The same yield was obtained at room temper-

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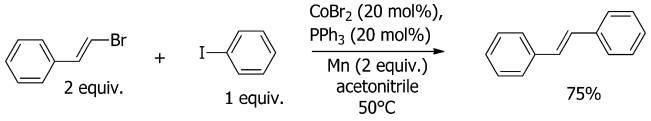
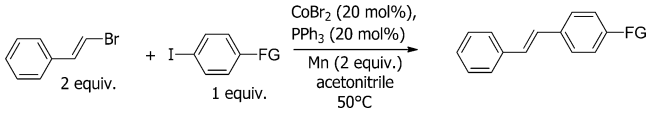
Scheme 1. Cobalt-Catalyzed Direct Vinylation of Phenyl Iodide with β-Bromostyrene



ature instead of 50 °C, but the reaction rate decreased (19 h instead of 3 h).

Then various aryl iodides reacted in these optimized conditions (Scheme 2). Results are reported in Table 1. Yields

Scheme 2. Cobalt-Catalyzed Direct Vinylation of Aryl Iodides with β-Bromostyrene



were good except for an activated aryl iodide such as methyl-4-iodoobenzoate. In this case, the dimerization of the starting material seems to be too rapid.

Table 1. Cobalt-Catalyzed Direct Vinylation of Aryl Iodides with β-Bromostyrene in One Pot: Substrate Scope

entry	ArI	yield[a] (%)	duration
1	*p*-MeOC$_6$H$_4$I	66	3 h
2	C$_6$H$_5$I	75	2 h 45
3	*p*-MeOCOC$_6$H$_4$I	(49)	45 min

[a]Isolated yield (GC yield).

We then envisaged the use of readily available poorly reactive aryl bromides (as opposed to the corresponding iodides) which would be a great extension of this reaction. In the previously optimized conditions with 2 equiv of β-bromostyrene, only 10% GC yield of styrene was detected. The two homocoupling products were formed in majority.

Satisfactory results were obtained by a dramatic change in the experimental conditions. In order to limit the dimerization of the more reactive halide (β-bromostyrene), it was added dropwise in the reaction mixture. By this procedure, β-bromostyrene remains in low concentration and cannot dimerize. Moreover, this allows us to remove the excess of the vinyl halide.

We then optimized many reaction parameters concerning the reaction between β-bromostyrene and ethyl 4-bromobenzoate (among them, the volume of solvent in which the β-bromostyrene is diluted and the duration of the addition), the screening of ligands was carried out, and the results are reported in Table 2.

Under the conditions described in Scheme 3, PPh_3 was replaced by some simple ligands, including 2,2′-bipyridine, dppp, dppe, and 1,4-bis(*m*-xylyl)-1,3-diazadiene. However, the most encouraging results were obtained with PPh_3.

The presence of a ligand was necessary (Table 2, entry 1), and the best one was commercial triphenylphosphine (Table 2, entry 2). It should be noted that the introduction of 2 equiv of triphenylphosphine did not lead to any improvement, and there was no significant difference with the preformed complex (Table 2 entry 3). With bidentate phosphine ligands, the aromatic halide reacted more slowly and the β-bromostyrene

Table 2. Effect of the Ligand on the Vinylation of Ethyl Bromobenzoate

entry	ligand	ArH[a] (%)	ArBr[a] (%)	ArVin[a] (%)	ArAr[a] (%)
1		12	0	27	61
2	PPh_3 (1 equiv)	1	0	55[b]	44
3	PPh_3 (2 equiv)[c]	16	40	30	14
4	dppe	9	15	53	23
5	dppp	18	70	16	0
6	bipyridine	28	0	8	64
7	diazadiene[d]	8	41	40	1

[a]GC yield. [b]Isolated yield. [c]Identical results with a preformed complex. [d]1,4-Bis(*m*-xylyl)-1,3-diazadiene.

dimerized (Table 2, entries 4 and 5). This effect is particularly enforced with dppp. Nitrogen ligands brought no improvement (Table 2, entries 6 and 7). Under these conditions (1 equiv of ArBr vs β-bromostyrene), yields were moderate even with PPh_3 due to the formation of ArAr. Thus, we have decided to introduce an excess of aryl halide (2 equiv vs β-bromostyrene), and we have extended the reaction to various bromides (Scheme 4, Table 3).

Satisfactory to very good yields were rapidly obtained under these conditions (the reaction was complete at the end of the addition). Remarkably, *ortho*-substituted aromatic compounds are especially well-suited for this reaction: their low reactivity in the dimerization reaction led to a better availability of this reagent for the cross-coupling reaction (Table 3, entries 3, 5, 8, and 12).

In the case of less reactive compounds such as β-chlorostyrene, diminution of the addition rate was required to allow reaction (Scheme 5). The cross-coupling of *p*-EtOCOC$_6$H$_4$Br or *p*-MeOC$_6$H$_4$Br with β-chlorostyrene led to similar isolated yields: 73% of the corresponding coupling products in 16 min or 72% in 20 min, respectively.

Aiming to study the stability of the double bond during the coupling process, we used the *cis*-β-bromostyrene prepared according to a previously described procedure.[31] A total retention of the double bond configuration was observed under these conditions (Scheme 6).

Mechanistic Studies. After this experimental study, we wanted to rationalize these results by a mechanistic study. The study was focused on the typical reaction of *trans*-β-bromostyrene (vinylic compound, represented by Vin-Br in schemes) with bromobenzene (aromatic compound, represented by Ph-Br in schemes). According to our previous mechanism on cobalt-catalyzed dimerization of aromatic halides,[32] involving a $Co^{II}(PPh_3)_2Br_2$, a catalytic cycle for this new reaction was expected. First, a preliminary reduction step of the Co^{II} precursor in Co^{I} active species is proposed. This species is then involved in an oxidative addition of a halide (either vinylic or aromatic) leading to a Co^{III} species, which is reduced in the following step by heterogeneous manganese to afford a new Co^{I} species that is involved in another oxidative addition with another halide (respectively with either aromatic or vinylic). The cycle is closed by a reductive elimination releasing both the Co^{I} catalytic species and the coupling product.

This mechanism accounts for the formation of three main products: the cross-coupling product (obtained by the consecutive oxidative addition of two different reagents in any order) and the dimers of each starting materials of the

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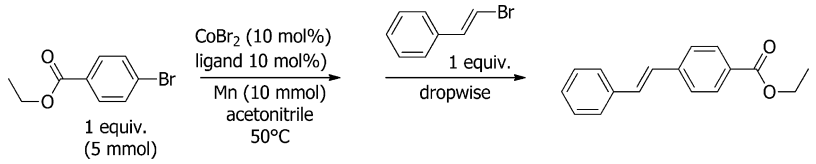
Scheme 3. Cobalt-Catalyzed Direct Vinylation of Phenyl Iodide with β-Bromostyrene



Scheme 4. Cobalt-Catalyzed Direct Vinylation of Aryl Bromides with β-Bromostyrene

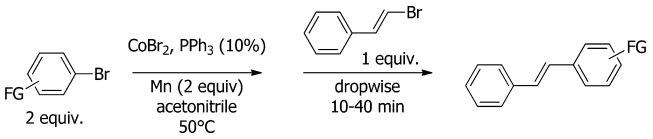
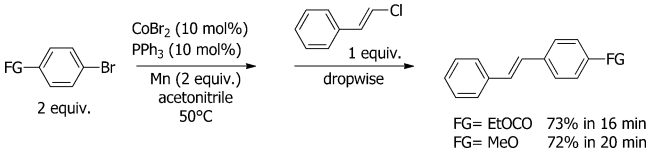


Table 3. Cobalt-Catalyzed Direct Vinylation of Various Aryl Bromides with β-Bromostyrene

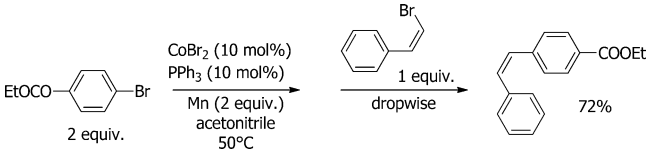
entry	ArBr	yield[a] (%)	duration (min)
1	*p*-EtOCOC$_6$H$_4$Br	68	10
2	*p*-CF$_3$C$_6$H$_4$Br	71	10
3	*o*-CF$_3$C$_6$H$_4$Br	84	30
4	*p*-CNC$_6$H$_4$Br	64	15
5	*o*-CNC$_6$H$_4$Br	82	10
6	*p*-Me-COC$_6$H$_4$Br	69	15
7	*p*-FC$_6$H$_4$Br	71	10
8	*o*-CH$_3$C$_6$H$_4$Br	74	40
9	C$_6$H$_5$Br	69	20
10	*p*-MeOC$_6$H$_4$Br	75	10
11	*m*-MeOC$_6$H$_4$Br	70	10
12	*o*-MeOC$_6$H$_4$Br	73	15

[a]Isolated yield.

Scheme 5. Cobalt-Catalyzed Direct Vinylation of Aryl Bromides with β-Chlorostyrene



Scheme 6. Cobalt-Catalyzed Direct Vinylation of Ethyl 4-Bromobenzoate with *cis*-β-Chlorostyrene



reaction (obtained by the addition of the same reagent twice on the metal center in a catalytic cycle).

In order to check our proposal, theoretical investigations were conducted. To achieve a good description of the system, a DFT-based study was initiated. DFT-based methods present a good compromise between the computation time required, the precision and the reliability of the results obtained in the study of metal-catalyzed reactions.[33] Many exchange-correlation functionals and basis set were evaluated to achieve the best characterization of our system. Two parameters were especially investigated such as the good reproduction of the structure obtained by X-ray diffraction for the [$CoBr_2(PPh_3)_2$] complex[34] and the good reproduction of spin states (see the Supporting Information for more details). A good reproduction of the geometry was achieved by some GGA exchange-correlation functionals. However, the best results were obtained by the use of the OPBE functional (GGA type, using the OPTX exchange functional[35] and the PBE correlation functional[36]). Moreover, this functional has given good results in the description of spin states of metal complexes as described with iron complexes[37] validating our choice. To save computation time, a two-level description procedure was used: optimization were realized using a D1 description level constituted by the Stuttgart–Dresden relativistic pseudopotential and associated basis set for cobalt, 6-31G* for all nonmetallic atoms except carbon and hydrogen not linked to phosphorus in phenyl rings which have been described by 3-21G*. Energies were then computed on the basis of these geometries with single-point computations using the D2 description level constituted of all-electron Def2-QZVP basis set for cobalt and 6-311+G** for all non metallic atoms. The solvent of the reaction (acetonitrile) was taken into account in single-point computations by a continuum model, using the C-PCM model as implemented in Gaussian 03 (see the Supporting Information for more precisions). This procedure is referred as OPBE/D2//OPBE/D1.

The first part of our work consisted of the study of the catalytic species. Preliminary computations show that optimization of a catalytic entity featuring two phosphines led to dissociation of one of the phosphine during the aryl bromide oxidative addition step. On the other hand, the addition of the vinyl bromide did not lead to the departure of one of the phosphines. These results lead us to two conclusions.

First, in the case of the reaction with dppp ligand or with 2 equiv of phosphines vs cobalt (where the two dimers are mostly obtained), the necessity for cobalt to be linked to two phosphines slows the oxidative addition of cobalt in the C–Br bond. Therefore, the vinyl halide dimerizes first, followed by the aryl halide, decreasing the cross-coupling yield.

Second, in the cases where a cross-coupling reaction takes place, another catalytic species should be proposed.

The complexity of the reaction mixture (involving both heterogeneous manganese and paramagnetic species such as cobalt) forbids an experimental study based on analytical methods such as NMR. Moreover, these systems are only sparsely studied. So, the literature did not give any clues to understand the nature of the species in our conditions. So we were bound to a purely theoretical investigation of the system. We proceeded to undertake an exhaustive study of [$CoBr_x(PPh_3)_n(MeCN)_m$] complexes (with $n + m \leq 3$ and $x = 1$ or 2) and found that when $x = 1$ and $x = 2$ the most stable complex is the heterobiliganded one: [$CoBr_x(PPh_3)(MeCN)$]. It indicates that the reduction of the most stable complex obtained leads to the most stable catalytic species. Thus, it seems reasonable to propose the involvement of [$CoBr(PPh_3)(MeCN)$] as the catalytic species.

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We then had to rule out some alternative mechanisms. First, a conceivable mechanism involving a intermediate RMnX species did not fit with the experimental conditions (the reaction conducted in the presence of acetic anhydride did not lead to any measurable amount of ketone),[38] which has already previously been described in our cobalt-catalyzed reductive process. Second, the possible involvement of radical species was both experimentally and theoretically investigated. Addition of galvinoxyl free radical in the medium did not change the reaction rate, and computation of the reaction energy (activation energy of this reaction was not computed) shows that the radical dissociation is about 10 kcal mol^{-1} over the activation energy of the oxidative addition proposed in our mechanism.

With these data in hand, we were able to compute the catalytic cycle using the previously modelization depicted above ([$CoBr(PPh_3)(MeCN)$] as initial active and PhCH=CHBr and PhBr as substrates). The reduction steps by manganese were not computed because of the difficult calculation of a probably heterogeneous process, but these steps are supposed to be fast and should not therefore be rate determining.

Calculations were carried out both for the triplet and singlet spin state. The computed data are given for the first oxidative addition in the cases of bromobenzene and β-bromostyrene (Figure 1) and a typical example for the reaction involving

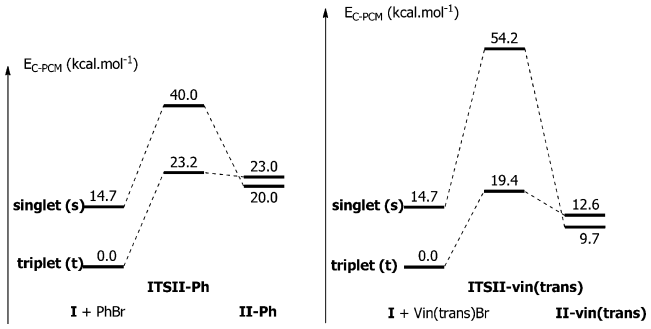

Figure 1. Energy profile in acetonitrile (C-PCM) for the first oxidative addition of respectively Ph-Br and Vin-Br on I.

successively the addition of bromobenzene and β-bromostyrene illustrating the second stage of the reaction (second oxidative addition from **III** and reductive elimination) (Figure 2). Converse to what we observed in the case of the dimerization of aryl halides, spin surfaces are very close to each other. These results led us to the determination of minimum energy crossing points (MECP) using the procedure described by Harvey.[39] The MECP were determined at the D2 level of description to ensure a good convergence of the geometry. We have been able to show that their presence did not have any influence on the reactivity (see the Supporting Information for more details) so for clarity they will not be represented in the following schemes.

Some general features are observed: the oxidative addition steps are the rate determining steps, the formation of the C−C bond is nearly barrierless, and it is the driving force of the reaction. These results are qualitatively the same than those obtained in our previous studies concerning the formation of biaryls.

The energy of the oxidative addition steps (from 7.7 to 23.2 kcal mol^{-1}) (see Figure 3) are low enough to account for the rapid reaction in the experimental conditions (50 °C).

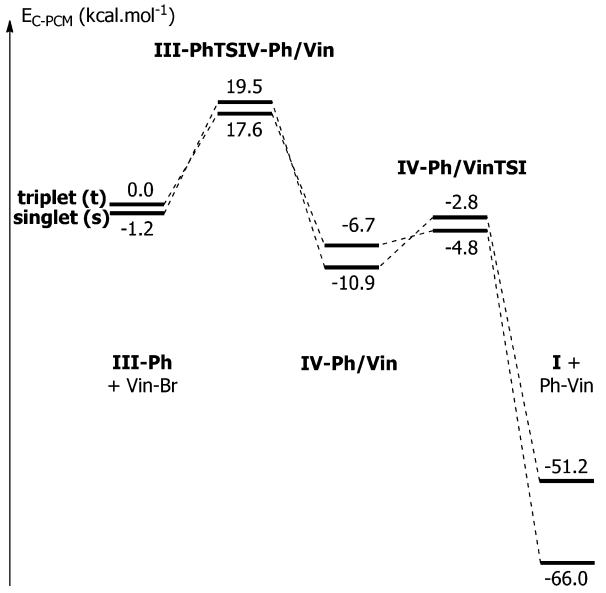

Figure 2. Energy profile in acetonitrile (C-PCM) for the second stage of the reaction from III-Ph to I (release of stilbene).

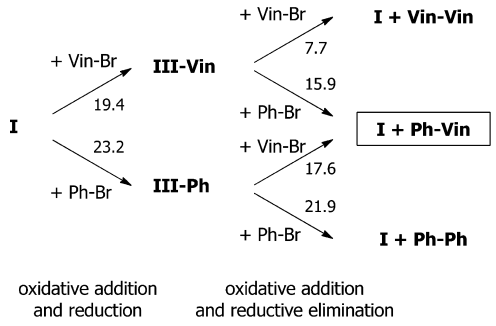

Figure 3. Schematic representation of the activation energies (C-PCM model, data in kcal mol^{-1}) for each stage of the reaction.

Moreover, the difference between the activation energies for the steps involving β-bromostyrene (e.g., 19.4 kcal mol^{-1} for the first oxidative addition) and bromobenzene (23.2 kcal mol^{-1} for the same step), respectively, reflects the difference of reactivity experimentally observed between these two species.

The second stage of the reaction (second oxidative addition and reductive elimination) was investigated from the two reduced products obtained after the first stage. The Figure 3 represents the four possible ways with the activation energies of each stage (first stage, first oxidative addition; second stage, second oxidative addition and reductive elimination). More details are given in the Supporting Information.

These results allow to explain the formation of the main products in the reaction conditions.

When all products in the medium are present in comparable concentrations (one-pot conditions), the most favorable pathway is the one with the lowest activation energies (upper pathway on the figure): it leads to the dimerization of the β-bromostyrene. Once the vinylic compound consumed, the bromobenzene dimerizes as it is the only reactant in the medium. This is consistent with our observations: under these conditions, very small amounts of cross-coupling products are obtained, the main products being the two dimers.

Conversely, when the vinylic compound is added dropwise, its concentration in the medium remain low which slows its

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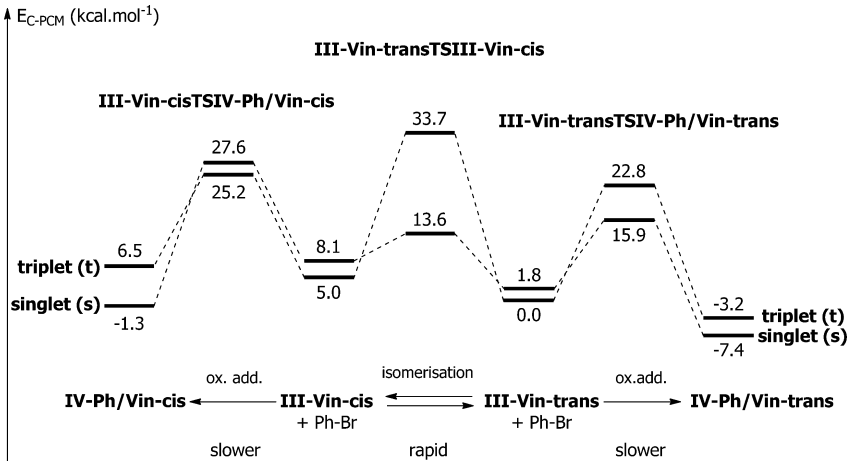


Figure 4. Energy profile in acetonitrile (C-PCM) for the comparative study of the isomerization of III-Vin and its transformation in IV.

oxidative addition. The addition of the aromatic moiety (in very large excess) on the catalyst is competitive in this case. This result is in line with the results previously published by Amatore, Jutand, and Torii[40] in the case of palladium-catalyzed reductive biaryls formation. Two pathways should account for the formation of the key complex [Co(Vin-*trans*)(Ph)Br]: either the consecutive addition of bromobenzene and *β*-bromostyrene or the reverse order.

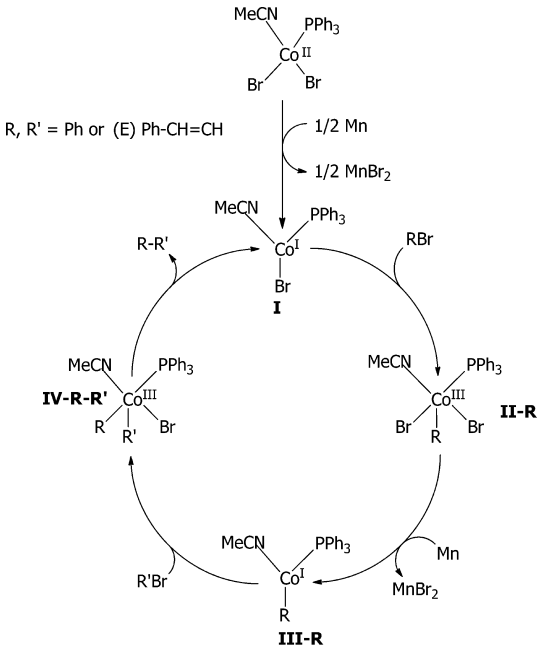
To discriminate between these two possibilities, we investigated the trans−cis isomerization of the cobalt−vinylic species [Co^{I}(Vin-*trans*)(PPh_3)(MeCN)]. If we assume that the first oxidative addition step entails the addition of bromostyrene, the cobalt−vinylic species [Co^{I}(Vin-*trans*)(PPh_3)(MeCN)] (**III-vin**) should be present after the first oxidative addition/reduction steps. A trans−cis isomerization could take place in this intermediate giving an isomer with a cis Co/Ph arrangement. The transition state for the isomerization of [Co^{I}(Vin-*trans*)(PPh_3)(MeCN)] to [Co^{I}(Vin-*cis*)(PPh_3)(MeCN)] was located. This activation barrier is low enough to allow isomerization (as for the mechanisms exposed earlier). Note that MECP were found, but their positions did not change the relative energies of the reactions involved.

This transition state (central one on the figure 4) is lower than those corresponding to the oxidative addition for both compounds and corresponds to a rapid reaction. As we have shown in the Experimental Section that no isomerization is observed during this reaction both from cis and trans compounds, the pathway involving the species allowing this [Co^{I}Vin(PPh3)(MeCN)] complex can be ruled out. It leads us to the result that in the case of dropwise addition of the vinylic species, the oxidative addition of the vinylic moiety follows the addition of the aromatic one, avoiding an intermediate in which isomerization should take place.

The involved mechanism in the dropwise conditions is then one of those starting from the **III-Ph** species. The formation of the cross-coupling product can be explained by the mechanism involving the oxidative addition of the aromatic compound and, in a second step, the addition of the vinylic fragment. The result involving the [Co^{I}Ph(PPh_3)(MeCN)] species is consistent with the presence in the reaction medium of the dimer of the aromatic species.

A corrected mechanism (involving MeCN instead of PPh_3 as ligand) for the cobalt-catalyzed reaction between bromobenzene and *β*-bromostyrene is reported in Scheme 7 according to our experimental and DFT studies.

Scheme 7. Corrected Mechanism for the Cobalt-Catalyzed Reaction between Bromobenzene and *β*-Bromostyrene



■ CONCLUSIONS

In conclusion, we have described a new and simple method for the preparation of stilbene derivatives by a reductive heterocoupling under cobalt catalysis. In this protocol, the procedure of addition of the reagents is crucial in determining the final coupling products.

The reaction can be carried out under mild conditions and affords satisfactory to very good yields. The total retention of the double bond was preserved. Moreover, the modelization of the reaction by DFT methods allowed us to propose two reaction pathways compatible with the experimental conditions depending on the experimental conditions. A good agreement was found between experimental results and mechanistic propositions.

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These new results encourage us to extend cobalt catalysis to diverse substrates in a near future.

EXPERIMENTAL SECTION

Typical procedure for the coupling of halostyrene with aryl bromide: to a solution of $CoBr_2$ (10 mol %, 0,25 mmol, 55 mg), triphenylphosphine (10 mol %, 0,25 mmol, 65 mg), and manganese powder (10 mmol, 550 mg) in acetonitrile (6 mL) was added at 50 °C aryl bromide (2 equiv, 5 mmol). A solution of bromostyrene (1 equiv, 2,5 mmol, 320 μL) in acetonitrile (2 mL) was added dropwise. Immediately after the addition began, the reaction mixture was vigorously stirred and trifluoroacetic acid (100 μL) added, causing a color change to dark gray. When the addition was over, the reaction mixture was hydrolyzed by hydrochloric acid (2 M) and extracted with dichloromethane. The organic layer was filtered and dried over $MgSO_4$. The amount of the cross-coupling product was measured by GC using an internal reference (tetradecane, 100 μL). The reaction was repeated for several addition rates, and the reaction with the best yield (reported in Table 3) was treated by evaporation of the solvent and purification by column chromatography on silica gel (petroleum ether/diethyl ether). The coupling product was characterized by NMR (^1H and ^{13}C).

(*E*)-Ethyl 4-styrylbenzoate:[41] colorless solid [CAS no. 109463-48-1] (0.429 g, 68%); ^1H NMR (300 MHz, $CDCl_3$) δ 8.06 (2H, d, *J* = 8.4 Hz), 7.59 (2H, d, *J* = 6.8 Hz), 7.56 (2H, d, *J* = 7.1 Hz), 7.41 (2H, t, *J* = 7.5 Hz), 7.33 (1H, m), 7.25 (1H, d, *J* = 16.2 Hz), 7.15 (1H, d, *J* = 16.6 Hz), 4.41 (2H, q, *J* = 7.1 Hz), 1.43 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 143.2, 138.2, 132.6, 131.5, 130.7, 130.3, 129.7, 129.1, 128.3, 127.8, 62.4, 15.9.

(*E*)-4-Trifluoromethylstilbene:[42] colorless oil [CAS no. 1149-56-0] (0.440 g, 71%); ^1H NMR (300 MHz, $CDCl_3$) δ 7.63 (3H, s), 7.56 (2H, d, *J* = 6.8 Hz), 7.54−7.27 (4H, m), 7.23 (1H, d, *J* = 16.4 Hz), 7.14 (1H, d, *J* = 16.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.2, 137.0, 131.6, 129.6 (q, *J* = 32.5 Hz), 129.2, 128.7, 127.5, 127.2, 127.0, 126.0 (q, *J* = 3.8 Hz), 124.7 (q, *J* = 268.1 Hz).

(*E*)-3-Trifluoromethylstilbene:[43] colorless oil (0.521 g, 84%); ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, 1H, *J* = 6.5 Hz), 7.66 (d, 1H, *J* = 6.6 Hz), 7.57−7.44 (m, 4H), 7.40−7.23 (m, 4H), 7.08 (d, 1H, *J* = 15.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.1, 136.6 (q, *J* = 2.4 Hz), 132.8, 132.0, 128.9, 128.3, 127.6 (q, J =29 Hz), 127.3, 127.2, 126.9, 125.8 (q, *J* = 5.8 Hz), 124.7 (q, *J* = 270 Hz), 124.5 (q, *J* = 1.9 Hz).

(*E*)-4-Styrylbenzonitrile:[44] colorless solid [CAS no. 13041-79-7] (0.328 g, 64%); ^1H NMR (300 MHz, $CDCl_3$) δ 7.62 (4H, q, *J* = 8.6 Hz), 7.56 (2H, d, *J* = 7.2 Hz), 7.48−7.31 (3H, m),7.24 (1H, d, *J* = 16.3 Hz), 7.11 (1H, d, *J* = 16.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.2, 136.7, 132.9, 132.8, 129.3, 129.1, 127.3, 127.3, 127.1, 119.5, 111.0.

(*E*)-2-Styrylbenzonitrile:[45] colorless oil [38175-96-1] (0.421 g, 82%); ^1H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, 1H, *J* = 8.0 Hz), 7.72−7.65 (m, 1H), 7.61−7.59 (m, 3H), 7.50−7.32 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.8, 136.4, 133.6, 133.3, 133.0, 128.6, 128.5, 127.4, 127.2, 125.5, 124.3, 111.5.

(*E*)-4-Acetylstilbene:[46] colorless solid [20488-42-0] (0.383 g, 69%); ^1H NMR (300 MHz, $CDCl_3$) δ 7.98 (2H, d, *J* = 8.4 Hz), 7.61 (2H, d, *J* = 8.6 Hz), 7.57 (2H, d, *J* = 8.0 Hz), 7.41 (2H, t, *J* = 7.7 Hz), 7.34 (1H, d, *J* = 7.2 Hz), 7.26 (1H, d, *J* = 16.3 Hz), 7.15 (1H, d, J =16.3 Hz), 2.64 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.3, 144.7, 139.4, 138.7, 134.2, 131.6, 131.6, 131.1, 130.2, 129.6, 129.2, 29.4.

(*E*)-4-Fluorostilbene:[47] colorless solid [CAS no. 718-25-2] (0.32 g, 71%); ^1H NMR (300 MHz, $CDCl_3$) δ 7.55−7.46 (m, 4H), 7.39 (t, 2H, *J* = 7.5 Hz), 7.29 (t, 1H, *J* = 7.4 Hz), 7.13−6.98 (m, 2H), 7.05 (d, 2H, *J* = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.5 (d, *J* = 242 Hz), 137.3, 133.6, 128.9, 128.6, 128.0 (d, *J* = 7.7 Hz), 127.7, 127.5, 126.5, 115.8 (d, *J* = 22 Hz).

(*E*)-2-Methylstilbene:[48] colorless oil [CAS no. 22257-16-5] (0.360 g, 74%); ^1H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, 1H, *J* = 7.0 Hz), 7.59 (d, 2H, *J* = 7.6 Hz), 7.46−7.38 (m, 3H), 7.33−7.22 (m, 4H), 7.06 (d, 1H, *J* = 16.2 Hz), 2.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 136.8, 136.1, 130.8, 130.3,129.0, 127.7, 127.6, 126.8, 126.5, 125.6, 20.4

(*E*)-Stilbene:[44] as a colorless solid [CAS no. 103-30-0] (0.311 g, 69%); ^1H NMR (300 MHz, $CDCl_3$) δ 7.62 (dd, 4H, *J* = 8.5 Hz, 1.3 Hz), 7.44 (tt, 4H, *J* = 7.3 Hz, 1.5 Hz), 7.34 (tt, 2H, *J* = 7.4 Hz, 1.3 Hz), 7.22 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5, 128.8, 128.7, 127.7, 126.7.

(*E*)-4-Methoxystilbene:[45] colorless solid [CAS no. 1694-19-5] (0.394 g, 75%); ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, 2H, *J* = 7.2 Hz), 7.46 (d, 2H, *J* = 8.6 Hz), 7.35 (t, 2H, *J* = 7.3 Hz), 7.24 (t, 1H, *J* = 7.2 Hz), 7.18 (d, 1H, *J* = 16.5 Hz), 6.98 (d, 1H, *J* = 16.4 Hz), 6.90 (d, 2H, J =8.7 Hz), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 137.8, 130.3, 128.7, 128.3, 127.8, 127.3, 126.6, 126.2, 114.0, 55.1.

(*E*)-3-Methoxystilbene:[47] colorless solid [CAS no. 14064-41-6] (0.368 g, 70%); ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, 2H, *J* = 7.2 Hz), 7.40−7.35 (m, 2H), 7.25 (m, 2H), 7.18−7.10 (m, 4H), 6.81 (d, 1H, *J* = 13.4 Hz), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8, 139.4, 137.7, 129.9, 129.0, 128.8, 128.5, 127.9, 126.9, 119.7, 113.8, 112.0, 55.7.

(*E*)-2-Methoxystilbene:[49] colorless oil [CAS no. 52805-92-2] (0.384 g, 73%); ^1H NMR (300 MHz, $CDCl_3$) δ 7.68 (dd, 1H, *J* = 7.8 Hz, 1.9 Hz), 7.62−7.58 (m, 3H), 7.45−7.29 (m, 4H), 7.17 (d, 1H, *J* = 16.4 Hz), 7.03 (t, 1H, *J* = 8.0 Hz), 6.98 (d, 1H, *J* = 8.1 Hz), 3.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5, 139.1, 129.8, 129.3, 129.1, 127.9, 127.0, 126.8, 126.7, 124.1, 121.3, 111.5, 56.1.

(*Z*)-Ethyl-4-styrylbenzoate:[50] colorless solid (0.454 g, 72%): ^1H NMR (300 MHz, $CDCl_3$) δ 7.91 (2H, d, *J* = 8.3 Hz), 7.35 (2H, d, *J* = 8.4 Hz), 7.26−7.20 (5H, m,), 6.75 (1H, d, *J* = 12.6 Hz), 6.64 (1H, d, *J* = 12.6 Hz), 4.39 (2H, q, *J* = 6.9 Hz), 1.43 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 142.5, 137.1, 132.2, 129.7, 129.4, 129.2, 129.0, 128.8, 128.5, 127.7, 61.3, 14.2.

ASSOCIATED CONTENT

Supporting Information

Copies of ^1H NMR and ^{13}C NMR spectra for all the compounds and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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