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Synthesis of *trans*-Disubstituted Alkenes by Cobalt-Catalyzed Reductive Coupling of Terminal Alkynes with Activated Alkenes

Subramaniyan Mannathan and Chien-Hong Cheng*[a]

Abstract: A cobalt-catalyzed reductive coupling of terminal alkynes, RC≡CH, with activated alkenes, R′CH=CH$_2$, in the presence of zinc and water to give functionalized *trans*-disubstituted alkenes, RCH=CHCH$_2$CH$_2$R′, is described. A variety of aromatic terminal alkynes underwent reductive coupling with activated alkenes including enones, acrylates, acrylonitrile, and vinyl sulfones in the presence of a CoCl$_2$/P(OMe)$_3$/Zn catalyst system to afford 1,2-*trans*-disubstituted alkenes with high regio- and stereoselectivity. Similarly, aliphatic terminal alkynes also efficiently participated in the coupling reaction with acrylates, enones, and vinyl sulfone, in the presence of the CoCl$_2$/P(OPh)$_3$/Zn system providing a mixture of 1,2-*trans*- and 1,1-disubstituted functionalized terminal alkene products in high yields. The scope of the reaction was also extended by the coupling of 1,3-enynes and acetylene gas with alkenes. Furthermore, a phosphine-free cobalt-catalyzed reductive coupling of terminal alkynes with enones, affording 1,2-*trans*-disubstituted alkenes as the major products in a high regioisomeric ratio, is demonstrated. In the reactions, less expensive and air-stable cobalt complexes, a mild reducing agent (Zn) and a simple hydrogen source (water) were used. A possible reaction mechanism involving a cobaltacyclopentene as the key intermediate is proposed.

Keywords: alkenes · cobalt · enyne coupling · ligands · reductive coupling

Introduction

Alkenes are useful compounds in a large number of synthetic applications and also found in the structure of numerous natural products and pharmaceutical agents.[1] In recognition of the importance of these compounds, their regio- and stereoselective preparation has been a great challenge, and many ingenious and selective methods have been devised over the years.[2] Nevertheless, there is still a need for a mild, convenient, and highly selective method for the synthesis of di-, tri-, and tetrasubstituted alkenes.

Transition-metal-catalyzed intermolecular coupling of alkynes and alkenes to regio- and stereoselectively give substituted alkenes is a highly atom-economic and environmentally friendly method in organic synthesis.[3] In this reaction, Alder-ene and reductive coupling products are of two familiar types. Trost's group extensively studied the intermolecular Alder-ene-type reaction of alkynes with alkenes for the synthesis of 1,4-dienes by using ruthenium complexes as the catalyst.[4] In 2002, we reported a cobalt-catalyzed intermolecular reductive coupling of internal alkynes with activated alkenes to afford trisubstituted alkenes by using water as the proton source and zinc as the reducing agent (Scheme 1 a).[5a] Since then, we have demonstrated the reductive coupling of various alkenes with different π components including different alkynes, alkenes, imines, allenes, and nitriles.[5b–i] An important finding from Montgomery's group involving nickel catalysis provided an efficient method for the reductive coupling of alkynes with enones, and alkynes with enals, to synthesize di- and trisubstituted alkenes (Scheme 1 b).[6] In the meantime, Micalizio et al. also reported a titanium alkoxide mediated bimolecular coupling of internal alkynes with unactivated alkenes to synthesize trisubstituted alkenes and polyenes (Scheme 1 c).[7] Recently, Hilt and Treutwein found an Alder-ene-type coupling of internal alkynes and terminal alkenes to afford 1,4-dienes in the presence of a cobalt catalyst.[8] In addition to these intermolecular versions, intramolecular reductive cyclization of enynes is also known in the literature.[5b,9] In this case, if terminal alkynyl groups were employed, the reductive cyclization products containing an *exo* 1,1-disubstituted instead of an *endo* 1,2-disubstituted alkenyl group were obtained.

In the reported metal-catalyzed intermolecular coupling reactions of alkynes with alkenes, the scope of alkynes was predominantly limited to internal alkynes. The coupling of internal alkynes with alkenes generally leads to trisubstituted alkenes (Scheme 1) and hence, the synthesis of *trans*-disubstituted alkenes remains demanding. Earlier reports from the literature illustrate that functionalized *trans*-disubstituted alkenes can also be obtained by conjugate addition of vinyl metal species to activated alkenes including enones and enoates.[10] These reactions required stoichiometric amounts of vinyl metal species that were prepared either by hydrometalation of terminal alkynes (zirconium is the most

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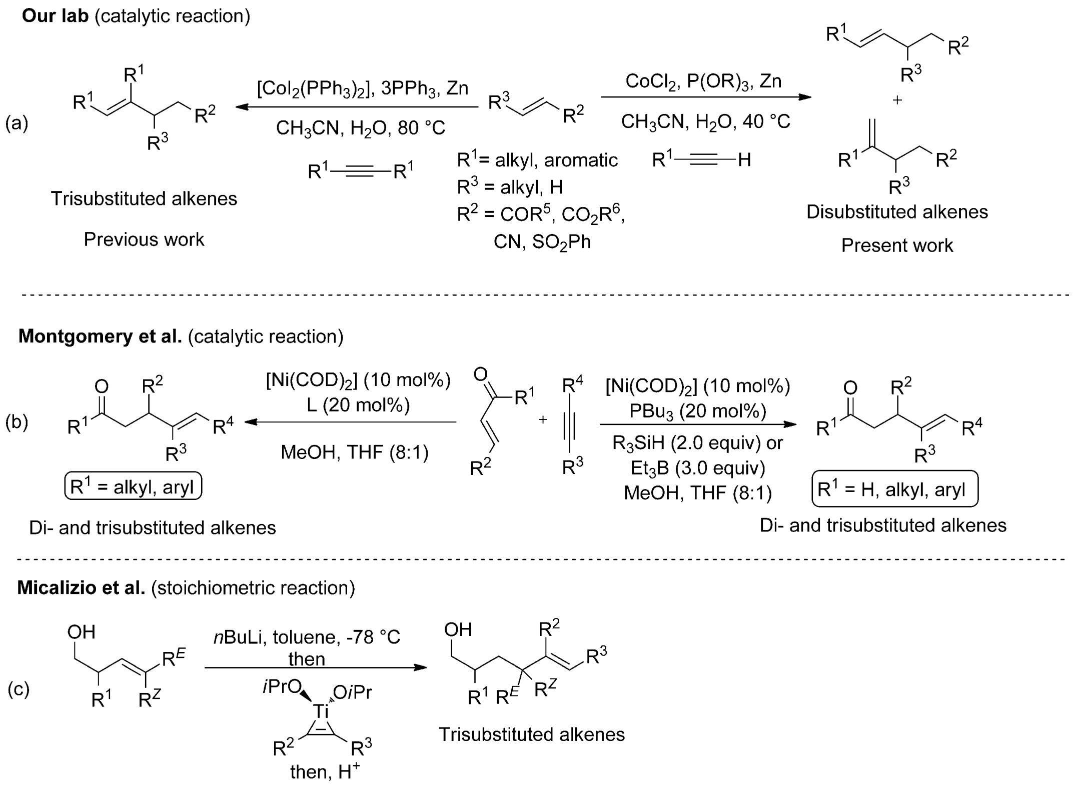


Scheme 1. Previous reports on the reductive coupling of alkynes with alkenes. COD = 1,5-cyclooctadiene.

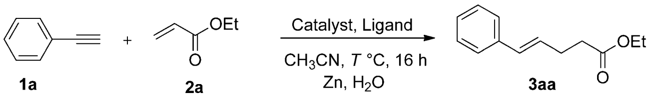
common) or metal–halogen exchange of vinyl halides.[11] Thus, it would be highly significant for organic synthesis if mild and convenient methods with a wide scope of substrates could be developed for the direct coupling of terminal alkynes with alkenes to synthesize stereoselective 1,2-disubstituted alkenes in one pot without utilizing either hydrometalation or a metal–halogen exchange strategy.[12]

Our continuing interest in the metal-catalyzed reductive coupling of π-components[5,13] prompted us to take the challenge to find a method for the intermolecular reductive coupling of terminal alkynes with activated alkenes. Herein, we report that cobalt complexes with suitable ligands can catalyze the reductive coupling of terminal alkynes and activated alkenes to give functionalized *trans*-disubstituted alkenes in good to excellent yields.[14]

Results and Discussion

Optimization studies: In the search for the effective catalytic conditions, we examined the reaction with various cobalt complexes (10 mol %) including [$CoI_2(PPh_3)_2$], [CoI_2(dppe)], [$CoCl_2(PPh_3)_2$], and [$CoCl_2$(dppe)] (dppe = 1,2-bis(diphenylphosphino)ethane; Table 1, entries 1 and 2). Unfortunately, all the phosphine complexes afforded only homocyclotrimerization products of **1a** and failed to provide the coupling product **3aa**. We then carried out the reductive coupling of **1a** and **2a** in the presence of simple cobalt(II) halides. To our surprise, $CoCl_2$ was effective, giving **3aa** in 8 % yield, but $CoBr_2$ and CoI_2 did not afford the reductive coupling product (Table 1, entries 3–5). Encouraged by this result, we next examined the reaction in the presence of various types of phosphine ligands with $CoCl_2$ (10 mol %). Among them, the electron-deficient monodentate phosphine ligands

Table 1. Effect of cobalt complexes on the reductive coupling of phenyl acetylene (**1a**) with ethyl acrylate (**2a**).[a]



1a **2a** **3aa**

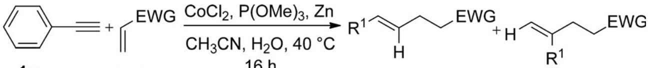
Entry	Catalyst	T [°C]	Ligand	Yield [%][b,c]
1	[$CoI_2(PPh_3)_2$]	80	3 PPh_3	–
2	[CoI_2(dppe)]	60	–	–
3	CoI_2	60	–	–
4	$CoBr_2$	60	–	–
5	$CoCl_2$	60	–	8
6	$CoCl_2$	60	5 P(2-furyl)$_3$	26
7	$CoCl_2$	60	5 $P(OPh)_3$	31
8	$CoCl_2$	60	5 P(O-*n*Bu)$_3$	40
9	$CoCl_2$	60	5 $P(OMe)_3$	61
10	$CoCl_2$	40	5 $P(OMe)_3$	93 (89)
11	CoI_2	40	5 $P(OMe)_3$	87
12	$CoCl_2$	40	2 $P(OMe)_3$	73

[a] Reaction conditions: phenylacetylene (**1a**; 1.00 mmol), ethyl acrylate (**2a**; 1.50 mmol), cobalt complex (0.10 mmol, 10 mol %), ligand (0.30–0.50 mmol, 30–50 mol %), Zn (2.75 mmol), H_2O (1.00 mmol), CH_3CN (2.00 mL), at 40–80 °C for 16 h. [b] Yields were measured from the crude products by the ^{1}H NMR spectroscopic integration method by using mesitylene as an internal standard. [c] Isolated yield is provided in parenthesis.

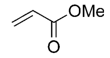
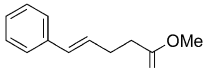
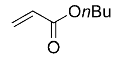
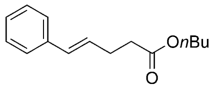
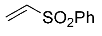
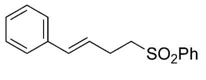
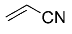
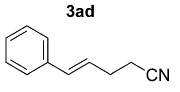
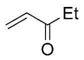
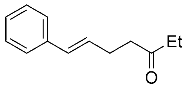
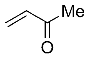
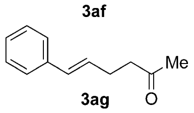
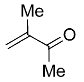
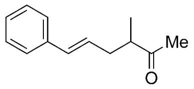
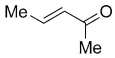
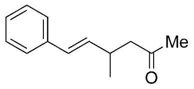
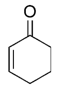
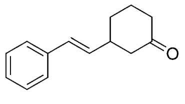
(50 mol %) P(2-furyl)$_3$, P(OPh)$_3$, P(O-*n*Bu)$_3$, and P(OMe)$_3$ were active in providing the reductive coupling product **3aa** in 26, 31, 40, and 61 % yields, respectively (Table 1, entries 6–9). In all these reactions, the homocyclotrimerization products of **1a** were observed as the major side products. To suppress these products and to increase the yield of **3aa**, the reaction was carried out at a lower temperature, 40 °C, for 16 h in the presence of P(OMe)$_3$ with CoCl$_2$. As expected, the reductive coupling product **3aa** was observed in 93 % ^{1}H NMR spectroscopic yield (89 % isolated yield) with a minor amount of the homotrimerization products of **1a** (Table 1, entry 10). A further decrease of the temperature led to lower yield. From these optimization studies, it is revealed that the reaction temperature and the nature of the phosphine ligand affect the product yield. Particularly, the coordination of the electron-deficient P(OMe)$_3$ ligand to the cobalt center plays a key role to suppress the formation of homotrimerization products of **1a** even at lower temperatures.

The reaction is highly regio- and stereoselective with the β-carbon atom of the acrylate group attached to the unsubstituted terminal alkyne carbon atom and the phenyl and (CH$_2$)$_2$CO$_2$Et groups are *trans* to each other. In this reaction, water acts as the proton source and zinc acts as the reducing agent. Based on these optimization studies, we chose the conditions CoCl$_2$ (10 mol %), P(OMe)$_3$ (50 mol %), Zn (2.75 mmol), and H$_2$O (1.00 mmol) in CH$_3$CN at 40 °C for 16 h for the reductive coupling of aromatic terminal alkynes with activated alkenes (Table 2).

Table 2. Results of cobalt-catalyzed reductive coupling of terminal alkyne **1a** with various activated alkenes **2a–j**.[a]



1a **2a–j** **3** **3'**

Entry	2	Product 3	Yield [%][b] (3/3′)
1	 **2b**	 **3ab**	85
2	 **2c**	 **3ac**	78
3	 **2d**	 **3ad**	85
4	 **2e**	 **3ae**	83[c]
5	 **2f**	 **3af**	87[c] (>95:5)
6	 **2g**	 **3ag**	90[c] (>95:5)
7	 **2h**	 **3ah**	91[d] (>95:5)
8	 **2i**	 **3ai**	85[d]
9	 **2j**	 **3aj**	89[d]

[a] Unless otherwise mentioned, all the reactions were carried out by using terminal alkynes **1** (1.00 mmol) and alkenes **2** (1.50 mmol) in the presence of CoCl$_2$ (10 mol %), P(OMe)$_3$ (50 mol %), Zn (2.75 mmol), and H$_2$O (1.00 mmol) in CH$_3$CN (2.00 mL) at 40 °C for 16 h. [b] Isolated yields; only regioisomer **3** was observed, unless otherwise mentioned. [c] The reaction was carried out in the presence of ZnI$_2$ (30 mol %). [d] AgSbF$_6$ (15 mol %) and ZnI$_2$ (15 mol %) were used instead of ZnI$_2$ (30 mol %).

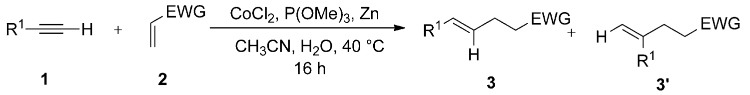
Reductive coupling of phenyl acetylene (1a) with activated alkenes (2b–j):[15] In addition to ethyl acrylate (**2a**), other acrylates, such as methyl acrylate (**2b**) and *n*-butyl acrylate (**2c**) under the optimized reaction conditions, also efficiently reacted with **1a** to provide reductive coupling products **3ab** and **3ac** in 85 and 78 % yields, respectively (Table 2, entries 1 and 2). To explore the scope of the reaction, we next examined the reaction of various activated alkenes **2d–j** with **1a** under the optimized reaction conditions (Table 2, entries 3–5). Phenyl vinyl sulfone (**2d**) provided the coupling product **3ad** in 85 % yield (Table 2, entry 3). Likewise, acrylonitrile (**2e**) also reacted with **1a** in the presence of a catalytic amount of ZnI$_2$ to afford **3ae** in 83 % yield (Table 2, entry 4). Without ZnI$_2$, product **3ae** was obtained only in 71 % yield.

Reaction of **1a** with ethyl vinyl ketone (**2f**) under the CoCl$_2$/P(OMe)$_3$ precatalyst system did not afford the reductive coupling product **3af**. However, in the presence of a catalytic amount of ZnI$_2$,[5b] the reaction proceeded well to furnish **3af** in 83 % yield (Table 2, entry 5). Notably, it also gave 1,1-disubstituted alkene **3af′** in approximately 4 % yield. Similarly, methyl vinyl ketone (**2g**) gave **3ag** in high yield (Table 2, entry 6). Substituted vinyl ketones, **2h** and **2i** also worked well providing coupling products **3ah** and **3ai** in 91 and 85 % yields, respectively (Table 2, entries 7 and 8). Likewise, cyclic enone 2-cyclohexenone (**2j**) participated to give **3aj** in 89 % yield (Table 2, entry 9). It is important to mention that for the reaction of **2h–j** a catalytic amount of AgSbF$_6$ and ZnI$_2$ is required to further improve the product yield. Without AgSbF$_6$, the products **3ah**, **3ai**, and **3aj** were obtained in 85, 75, and 82 % yields, respectively. The presence of AgSbF$_6$ and ZnI$_2$ are essential for this reaction, which indicates that a cationic cobalt complex works as an active catalytic species. It is necessary to point out that the application of a silver salt in the present reductive coupling reaction is restricted only to substituted enones, whereas in the case of unsubstituted enones, no improvement in the yield was observed. It is noteworthy that the present catalytic reductive coupling reaction is applied to various alkenes including vinyl ketones, acrylates, acrylonitrile, and vinyl sulfone, whereas in the reported nickel-catalyzed reductive coupling reaction, only enones and enals were demonstrated.[6c]

Reductive coupling of terminal alkynes (1b–q) with activated alkenes (2b–j): To evaluate the scope of the reductive coupling reaction of terminal alkynes with alkenes, we examined a range of aromatic terminal alkynes under the optimized reaction conditions. As expected, the $CoCl_2$/$P(OMe)_3$ system showed good compatibility with both halo-substituted and electron-donating-group-substituted aromatic terminal alkynes (**1b**–**e**) affording the respective products (**3bf**, **3cf**, **3dg**, and **3ed**) in good to excellent yield (Table 3, entries 1–4). Correspondingly, *para*-tolylacetylene (**1f**) gave the product **3fa** in 92% yield (Table 3, entry 5). 2-Ethynyl-6-methoxynaphthalene (**1g**) provided the disubstituted alkene **3gb** in 82% yield (Table 3, entry 6). Heteroaromatic alkyne 3-ethynylthiophene (**1h**) coupled with **2f** to furnish **3hf** in good yield (Table 3, entry 7). Similarly, disubstituted aromatic terminal alkynes including **1i**, **1j**, and **1k** provided the corresponding products **3if**–**kf** in 85–91% yields (Table 3, entries 8–10).

Aliphatic terminal alkynes also successfully participated in the reductive coupling reactions. However, a different combination of $CoCl_2$ (10 mol%) with triphenyl phosphite $P(OPh)_3$ (20 mol%) is required to achieve the coupling reaction in high product yield. Thus, the reaction of 1-hexyne (**1l**) with acrylate (**2a**) in the presence of the $CoCl_2$/$P(OPh)_3$ system afforded regioisomeric reductive coupling products **3la**/**3la′** in 85% isolated yield in a 50:50 regioisomeric ratio (Table 3, entry 11). Excitingly, when 1-hexyne (**1l**) was treated with 2-cyclohexenone (**2j**), a better regioselectivity of **3lj**/**3lj′** was observed, that is, an 87:13 ratio, with 82% yield (Table 3, entry 12). In a similar fashion, bulkier aliphatic alkyne, 3,3′-dimethyl-1-butyne (**1m**) furnished 1,2-*trans*-disubstituted alkene **3mj** exclusively in 87% yield (Table 3, entry 13). An aliphatic terminal alkyne bearing a functional group was also tolerated in the reaction. Thus, hex-5-yn-1-ol (**1n**) reacted with **2f** to give the respective coupling products **3nf**/**3nf′** in 88% yield with a regioisomeric ratio of 50:50 (Table 3, entry 14). Enynes effectively participated in the reductive coupling reaction and afforded 1,3-dienes in nearly single regioisomeric form. For example, 1-ethynyl cyclohexene (**1o**) and 2-methylbut-1-en-3-yne (**1p**) underwent highly regioselective coupling with **2d** to

Table 3. Results of cobalt-catalyzed reductive coupling of terminal alkynes **1a**–**p** with various activated alkenes **2a**–**j**.[a]



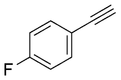
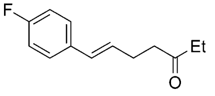
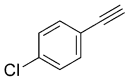
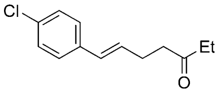
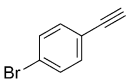
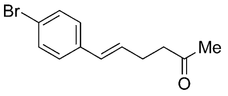
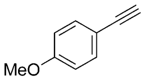
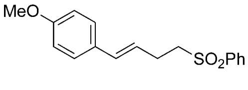
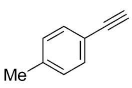
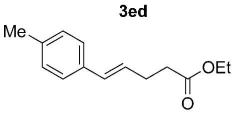
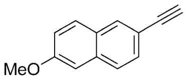
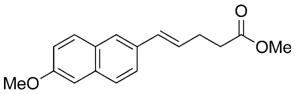
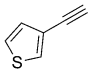
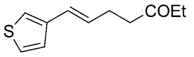
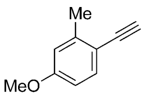
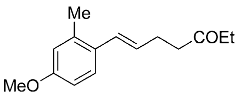
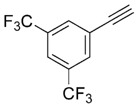
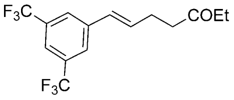
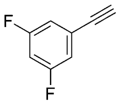
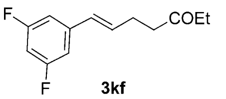
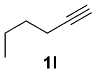
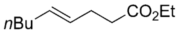
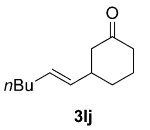
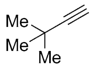
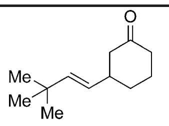
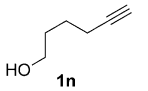
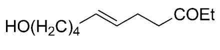
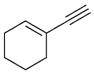
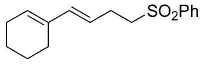
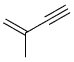
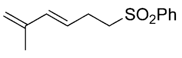
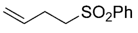
Entry	1	2	Product 3	Yield [%][b] (3/3′)
1	 **1b**	**2f**	 **3bf**	94[c] (>95:5)
2	 **1c**	**2f**	 **3cf**	91[c] (>95:5)
3[f]	 **1d**	**2g**	 **3dg**	83[c] (>95:5)
4	 **1e**	**2d**	 **3ed**	88
5	 **1f**	**2a**	 **3fa**	92
6	 **1g**	**2b**	 **3gb**	82
7	 **1h**	**2f**	 **3hf**	88[c] (>95:5)
8	 **1i**	**2f**	 **3if**	85[c] (>95:5)
9	 **1j**	**2f**	 **3jf**	87[c] (>95:5)
10	 **1k**	**2f**	 **3kf**	91[c] (>95:5)
11[d]	 **1l**	**2a**	 **3la**	85 (50:50)
12[d]	**1l**	**2j**	 **3lj**	82[e] (87:13)

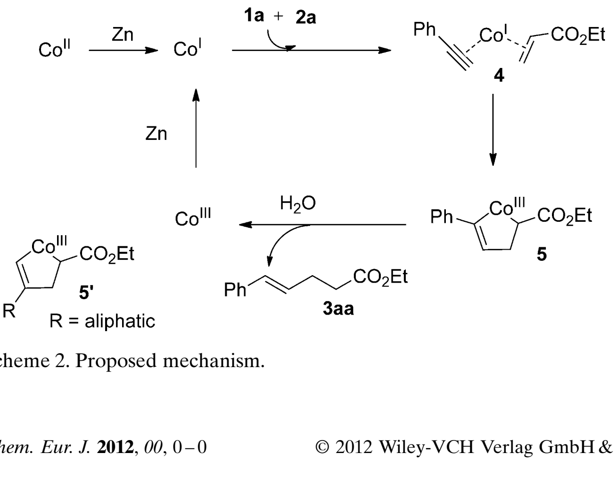
Table 3. (Continued)

Entry	1	2	Product 3	Yield [%][b] (3/3′)
13[d]	 **1m**	**2j**	 **3mj**	87[e]
14[d]	 **1n**	**2f**	 **3nf**	88[c] (50:50)
15[d]	 **1o**	**2d**	 **3od**	87 (>95:5)
16[d]	 **1p**	**2d**	 **3pd**	92 (>95:5)
17[d]	H—≡—H **1q**	**2d**	 **3qd**	77

[a] Unless otherwise mentioned, all the reactions were carried out by using terminal alkynes **1** (1.00 mmol) and alkenes **2** (1.50 mmol) in the presence of $CoCl_2$ (10 mol%), $P(OMe)_3$ (50 mol%), Zn (2.75 mmol), and H_2O (1.00 mmol) in CH_3CN (2.00 mL) at 40°C for 16 h. [b] Isolated yields; only regioisomer **3** was observed, unless otherwise mentioned. [c] The reaction was carried out in the presence of ZnI_2 (30 mol%). [d] For entries 11–17, $P(OPh)_3$ (20 mol%) was used as the ligand instead of $P(OMe)_3$. [e] $AgSbF_6$ (15 mol%) + ZnI_2 (15 mol%) were used instead of ZnI_2 (30 mol%). [f] A trace amount of debrominated reductive coupling product was also observed.

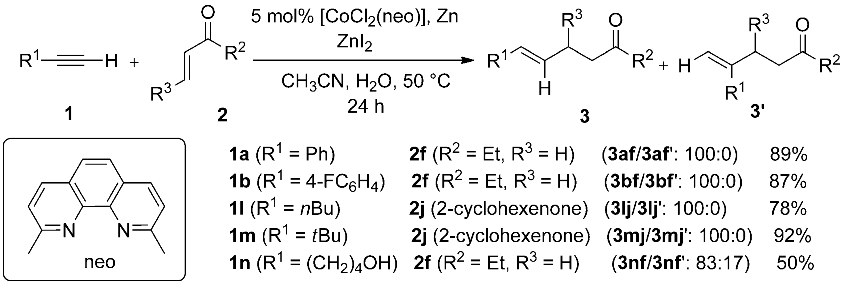
give **3od** and **3pd** in 87 and 92% yield, respectively, with a regioisomeric ratio of >95:5 (Table 3, entries 15 and 16). Finally, the scope of the reaction was extended by coupling **2d** with acetylene gas (**1q**) to afford the terminal alkene **3qd** in 77% yield (Table 3, entry 17).

Proposed mechanism: A possible reaction mechanism for the present cobalt-catalyzed reductive coupling reaction is proposed in Scheme 2. The catalytic reaction is likely initiated by the reduction of Co^{II} to Co^{I} by Zn dust. Coordination of **1a** and **2a** to the Co^{I} center followed by oxidative cyclization then gives cobaltacyclopentene intermediate **5**. Protonation of **5** by water affords reductive coupling product **3aa** and a Co^{III} species that is reduced by Zn to generate Co^{I}. A similar reaction mechanism is also expected for the reductive coupling of other terminal alkynes with alkenes. Intermediate **5′** accounts for the formation of products **3′**.



Scheme 2. Proposed mechanism.

Reductive coupling of terminal alkynes (1) with enones (2) by using [$CoCl_2$(neo)]: During the course of our investigation on reductive coupling of terminal alkynes with alkenes, we found that the phosphine-free cobalt catalyst system [$CoCl_2$(neo)][16] (neo = neocuproine = 2,9-dimethyl-1,10-phenanthroline) effectively catalyzed the reductive coupling of terminal alkynes with enones, affording 1,2-*trans*-disubstituted alkenes as the major products in a high regioisomeric ratio (Scheme 3, and see Table 2 for the structures). This catalyst system significantly decreased the catalyst loading to 5 mol% and afforded the 1,2-*trans* disubstituted alkenes **3kj** and **3lj** exclusively in single isomeric form. Moreover, it also shows high regioselectivity for the coupling of aromatic terminal alkynes with enones. However, the [$CoCl_2$(neo)] system is limited only to enones and it is not suitable for the coupling of terminal alkynes with acrylates, acrylonitrile, and vinyl sulfone.



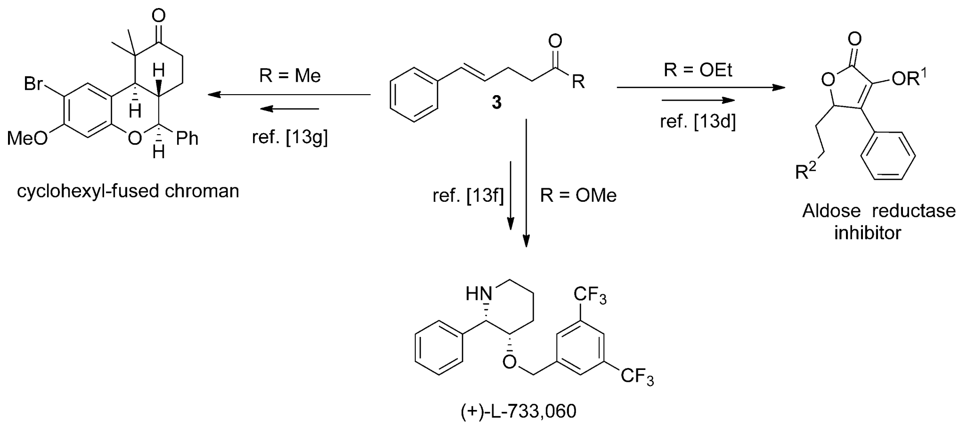
1a (R^1 = Ph)	**2f** (R^2 = Et, R^3 = H)	(**3af**/**3af′**: 100:0)	89%
1b (R^1 = 4-FC_6H_4)	**2f** (R^2 = Et, R^3 = H)	(**3bf**/**3bf′**: 100:0)	87%
1l (R^1 = *n*Bu)	**2j** (2-cyclohexenone)	(**3lj**/**3lj′**: 100:0)	78%
1m (R^1 = *t*Bu)	**2j** (2-cyclohexenone)	(**3mj**/**3mj′**: 100:0)	92%
1n (R^1 = $(CH_2)_4OH$)	**2f** (R^2 = Et, R^3 = H)	(**3nf**/**3nf′**: 83:17)	50%

Scheme 3. Synthesis of 1,2-*trans*-disubstituted alkenes by using [$CoCl_2$(neo)] as the catalyst system.

The functionalized *trans*-disubstituted alkenes obtained from the present cobalt-catalyzed reductive coupling reaction are highly useful synthetic intermediates in organic synthesis and their applications in various organic transformation reactions are well known in literature (Scheme 4).[17]

Conclusion

We have successfully developed a synthetically very useful cobalt-catalyzed reductive coupling of terminal alkynes with activated alkenes to provide various *trans*-disubstituted al-



Scheme 4. Organic transformation reactions of functionalized *trans*-disubstituted alkenes.

kenes in good to excellent yields. In the reaction, less expensive and air-stable cobalt catalysts, a very mild reducing agent (Zn), and one of the simplest hydrogen sources (water) were used. The present catalytic reaction is successfully applied to a wide range of alkenes, such as vinyl ketones, acrylonitrile, acrylates, and vinyl sulfone, and also to both aromatic and aliphatic terminal alkynes. In addition, we have demonstrated a phosphine-free cobalt catalyst system for the reductive coupling of terminal alkynes with enones to synthesize 1,2-*trans*-disubstituted alkenes in high regio- and stereoselectivity. Overall, we believe that the present manuscript represents a great advance to the chemistry of enyne coupling reactions.

Experimental Section

General procedure for the reductive coupling of aromatic terminal alkynes with acrylates and vinyl sulfone: A sealed tube (20 mL) containing $CoCl_2$ (0.10 mmol, 10 mol%) and zinc powder (2.75 mmol) was evacuated and purged with nitrogen gas three times. Freshly distilled CH_3CN (2.0 mL) and $P(OMe)_3$ (0.50 mmol, 50 mol%) were added and the mixture was stirred until the solution became green. Then, the alkyne (1.00 mmol), acrylate or vinyl sulfone (dissolved in 0.50 mL of CH_3CN; 1.20 mmol), and H_2O (1.00 mmol) were sequentially added by syringe. The reaction mixture was stirred at 40 °C for 16 h and was then cooled, diluted with dichloromethane, and stirred in air for 10 min. The mixture was filtered through a Celite and silica gel pad and washed with dichloromethane. The filtrate was concentrated to afford the crude alkene. The ratio of regioisomers was determined by ^1H NMR spectroscopic analysis of the unpurified sample. Later, the crude residue was purified on a silica gel column by using *n*-hexane/ethyl acetate as the eluent to afford the desired product **3**.

For the coupling of aromatic terminal alkynes with acrylonitrile or enones, the reaction was carried out by using $CoCl_2$ (0.100 mmol, 10 mol%), $P(OMe)_3$ (0.500 mmol, 50 mol%), Zn powder (2.75 mmol), ZnI_2 (0.300 mmol, 30 mol%), and H_2O (1.00 mmol) in CH_3CN (2.0 mL) at 40 °C for 16 h.

A similar reaction procedure was followed for the reaction of aliphatic terminal alkynes (1.50 mmol) with activated alkenes (1.00 mmol), such as acrylate, vinyl sulfone, and enone, but a different ligand $P(OPh)_3$ (0.200 mmol, 20 mol%) was used instead of $P(OMe)_3$. For enones, a catalytic amount of ZnI_2 (0.300 mmol, 30 mol%) was used. The ratio of regioisomers was determined by ^1H NMR spectroscopic analysis of the unpurified sample.

For the coupling of acetylene gas with vinyl sulfone, the reaction was carried out by using $CoCl_2$ (0.100 mmol, 10 mol%), $P(OPh)_3$ (0.200 mmol, 20 mol%), Zn powder (2.75 mmol), and H_2O (1.00 mmol) in the presence of an acetylene atmosphere (1 atm) in CH_3CN (2.0 mL) at 60 °C for 16 h.

Acknowledgements

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Ligands

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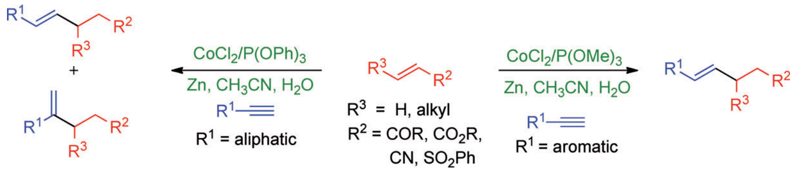
Synthesis of *trans*-Disubstituted Alkenes by Cobalt-Catalyzed Reductive Coupling of Terminal Alkynes with Activated Alkenes



Activate your alkenes! Cobalt complexes with suitable ligands catalyze the reductive coupling of terminal alkynes with activated alkenes in the presence of zinc and water to give 1,2-*trans*-disubstituted alkenes in good to excellent yields (see scheme).