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Regio- and Enantioselective Cobalt-Catalyzed Reductive [3+2] Cycloaddition Reaction of Alkynes with Cyclic Enones: A Route to Bicyclic Tertiary Alcohols[**]

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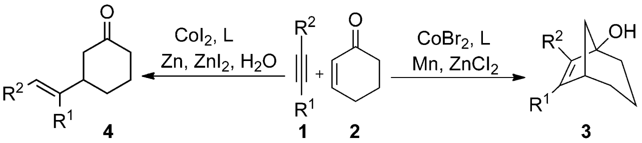
Cycloaddition reactions are among the most powerful and widely applied methods for the synthesis of carbo- and heterocycles in organic synthesis.[1] Transition-metal-catalyzed cycloaddition reactions are particularly attractive because they can provide new opportunities for the synthesis of various cyclic molecules in one pot.[2] These reactions become possible as the complexation of substrates to metal temporarily polarizes and activates otherwise unreactive species.[3] Some recent developments in this field are metal-catalyzed reductive [3+2] cycloaddition reactions utilizing α,β-unsaturated carbonyl compounds as the three-carbon unit. Sato et al. reported a stoichiometric titanium-promoted addition of tethered alkynes and enoates to synthesize bicyclic ketones.[4] The work of Montgomery and co-workers on stoichiometric nickel-promoted addition of tethered alkynes and enals showed that the [3+2] cyclization can also be achieved using enolate metallacycles.[5] Later, they disclosed a catalytic intermolecular version of the cycloaddition of alkynes and enals to synthesize cyclopentenols and cyclopentenones using triethylborane as the reducing agent.[6a,b] In 2007, we reported a cobalt-catalyzed diastereoselective reductive [3+2] cycloaddition of allenes and enones affording 3-methylene cyclopentanol derivatives.[7a] Subsequently, Urabe and co-workers described an iron-mediated intramolecular reductive cyclization of dienedioates to synthesize bicyclic ketoesters.[8] Very recently, Ogoshi and Ohashi developed a unique Ni^0-catalyzed [3+2] cycloaddition reaction of α,β-unsaturated phenyl esters with alkynes in *i*PrOH to yield cyclopentenone derivatives.[9]

We have been interested in the reductive coupling of π components[10] and related cycloaddition reaction.[11] Herein, we report a novel cobalt-catalyzed reductive [3+2] cycloaddition of cyclic enones and alkynes affording bicyclic tertiary alcohols[12] in good to high regioselectivity. Moreover, the asymmetric version[13] of this catalytic reaction leading to two stereogenic centers can also be achieved by the proper choice of a chiral ligand (Scheme 1). This catalytic reaction provides an atom-economic method[14] for the synthesis of sterically crowded bicyclic tertiary alcohols, an important motif present in *Galbulimima* alkaloids,[15] under mild conditions using relatively inexpensive cobalt metal complexes as catalysts.



Scheme 1. Cobalt-catalyzed intermolecular reductive coupling and [3+2] cycloaddition reaction of enones with alkynes. L = ligand.

Recently, we reported the enantioselective reductive coupling of alkynes with cyclic enones to synthesize β-substituted ketones in good yields and with high *ee* values.[16] In the course of the study, we found that the reaction of diphenylacetylene (**1a**) with 2-cyclohexenone (**2a**) in the presence of $CoBr_2$ (5.0 mol %), 1,2-bis(diphenylphosphino)ethane (dppe; 5.0 mol %), Mn (1.10 mmol), $ZnCl_2$ (0.20 mmol), and CH_3CN at 40 °C for 24 h, gave the bicyclic product **3a** in 86 % yield (Table 1, entry 1). Solvent played a vital role for the success of the reaction: CH_3CN and 1,4-dioxane afforded **3a** in 86 % and 31 % yield, respectively, whereas THF, CH_2Cl_2, and toluene were totally inactive. Control experiments revealed that the reaction did not proceed without $CoBr_2$/dppe, Mn, or $ZnCl_2$. Furthermore, we found that **4a**, the reductive coupling product from **1a** and **2a**, could not be converted into product **3a** under the reaction conditions, which suggests that **4** is not an intermediate of **3a** (Scheme 1). To further understand the catalytic conditions, we examined this catalytic reaction in the presence of various cobalt complexes (see the Supporting Information) as the catalyst. Among them, CoI_2/dppe, CoI_2/dppp (dppp = 1,3-bis(diphenylphosphino)propane), $CoI_2/P(OMe)_3$, and $CoI_2/P(OPh)_3$ were active, but provided **3a** in low yield (27–38 %). We also found that CoI_2 (5.0 mol %), *rac*-2,2′-bis-1,1′-binaphthyl (*rac*-binap; 5.0 mol %), Zn (1.10 mmol), ZnI_2 (0.20 mmol), in 1,4-dioxane was active, affording **3a** in 93 % yield.

To investigate the scope of the cycloaddition reaction, various alkynes **1b–j** were reacted with **2a** using the $CoBr_2$/dppe, Mn, $ZnCl_2$ system (Table 1, entries 2–10). Thus, di-*p*-tolylacetylene (**1b**) and di-*p*-chlorophenylacetylene (**1c**) underwent cycloaddition to give **3b** and **3c** in 96 and 85 % yield, respectively (entries 2 and 3). In contrast, di-*p*-bromophenylacetylene (**1d**) afforded product **3d** in low yield (entry 4). Heteroaromatic alkyne, **1e** successfully partici-

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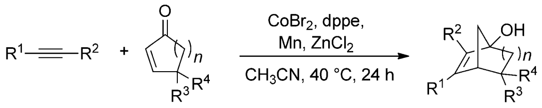
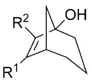
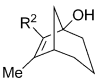
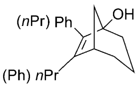
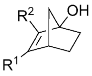
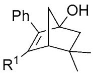
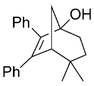
Table 1: Reductive [3+2] cycloaddition of alkynes with cyclic enones.[a]



1a–k **2a–d** **3a–p**

2a: $n = 2$, R^3, R^4 = H **2b**: $n = 1$, R^3, R^4 = H
2c: $n = 1$, R^3, R^4 = Me **2d**: $n = 2$, R^3, R^4 = Me

Entry	1	2	Product 3		Yield [%][b,c]
1	**1a**	**2a**		**3a**: R^1,R^2 = Ph	86 (93)
2	**1b**	**2a**		**3b**: R^1,R^2 = 4-MeC_6H_4	96 (97)
3	**1c**	**2a**		**3c**: R^1,R^2 = 4-ClC_6H_4	85 (87)
4	**1d**	**2a**		**3d**: R^1,R^2 = 4-BrC_6H_4	21 (75)
5	**1e**	**2a**		**3e**: R^1,R^2 = 2-thienyl	74 (76)
6	**1f**	**2a**		**3f**: R^1,R^2 = *n*-propyl	85 (83)
7	**1g**	**2a**		**3g**: R^2 = Ph	93 (88)
8	**1h**	**2a**		**3h**: R^2 = 4-biphenyl	92 (91)
9	**1i**	**2a**		**3i**: R^2 = naphthyl	90 (93)
10	**1j**	**2a**		**3j**: R^2 = 3-$MeOC_6H_5$	81 (0)
11[d,e]	**1k**	**2a**		**3k** (**3k′**)	78 (32)
12	**1a**	**2b**		**3l**: R^1,R^2 = Ph	87 (84)
13	**1b**	**2b**		**3m**: R^1,R^2 = 4-MeC_6H_4	92 (91)
14	**1a**	**2c**		**3n**: R^1 = Ph	83 (77)
15	**1g**	**2c**		**3o**: R^1 = Me	86 (81)
16	**1a**	**2d**		**3p**	70 (0)

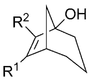
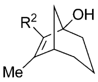
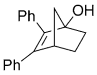
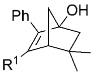
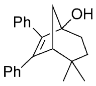
[a] Unless otherwise mentioned, all reactions were carried out using alkyne **1** (0.40 mmol) and alkene **2** (0.60 mmol) in the presence of $CoBr_2$ (5.0 mol%), dppe (5.0 mol%), Mn (1.10 mmol), $ZnCl_2$ (0.20 mmol) in CH_3CN at 40 °C for 24 h. [b] Yield of isolated product. [c] Data in parentheses are yields of reactions carried out using CoI_2 (5.0 mol%), *rac*-binap (5.0 mol%), Zn (1.10 mmol), and ZnI_2 (0.20 mmol) in 1,4-dioxane (0.80 mL) at 40 °C for 24 h. [d] The regioisomeric ratio of **3k**/**3k′** is 75:25. [e] Reaction was carried out at 60 °C.

pated in the reaction to provide **3e** in 74% yield (entry 5) and the aliphatic alkyne 4-octyne (**1f**) gave cycloadduct **3f** in good yield (entry 6). Unsymmetrical alkynes also underwent reductive cycloaddition, providing the corresponding bicyclic compounds with good to high regioselectivity (entries 7–11). Thus, 1-phenyl-1-propyne (**1g**) coupled with **2a** to provide **3g** in 93% yield (entry 7). Similarly, **1h–j** gave the respective cycloadducts, **3h–j**, in good to excellent yield (entries 8–10). 1-Phenyl-1-pentyne (**1k**) also participated in the reaction, providing bicyclic product **3k**/**3k′** in a regioisomeric ratio of 75:25 (entry 11). Unfortunately, silyl-substituted alkynes did not furnish any [3+2] cycloadducts with **2a**. The present reductive [3+2] cycloaddition reaction is not suitable for terminal alkynes,[10f] but instead leads to facile homocyclotrimerization of alkynes under the optimized reaction conditions.

The present catalytic reaction was successfully extended to various cyclic enones, **2b–d** (Table 1, entries 11–15). Thus, 2-cyclopentenone (**2b**) reacted with **1a** and **1b**, providing **3l** and **3m** in 87 and 92% yield, respectively (entries 12 and 13). Similarly, 4,4-dimethyl-substituted cyclopentenone (**2c**) reacted with **1a** and **1g** to afford the respective products, **3n** and **3o**, in good yields (entries 14 and 15). Likewise, **2d** provided **3p** in 70% yield (entry 16). On the other hand, 2-cycloheptenone and acyclic enones did not afford any [3+2] cycloadducts with **1** under the standard reaction conditions. The catalytic reactions can also be carried out using the CoI_2/*rac*-binap, Zn, ZnI_2 system with 1,4-dioxane as the solvent to give similar product yields (see Table 1).

Having successfully established the reductive [3+2] cycloaddition reaction, we then studied the asymmetric version of the reaction (Table 2). After systematic evaluation of various chiral ligands using **1a** and **2a** as model substrates in the presence of CoI_2 (5.0 mol%), Zn (1.10 mmol), and ZnI_2 (0.20 mmol) at room temperature with CH_3CN as the solvent, we found that (*R*,*R*,*S*,*S*)-2,2′-Di-*tert*-butyl-2,3,2′,3′-tetrahydro-1*H*,1′*H*-(1,1′)biisophosphindolyl (Duanphos) was the most effective chiral ligand, affording product **3a** in 71% yield with 90% *ee*. Other chiral ligands, such as (*R*)-binap and its derivatives, including (*R*)-H_8-binap and (*S*)-Tol-binap, were also active, providing **3a** in good yields and moderate *ee*. On the other hand, at a slightly higher reaction temperature (40 °C), (*R*)-1-(2-diphenylphosphino-1-naphthyl)isoquinoline (quinap) afforded **3a** with 96% *ee* and moderate yield. The absolute configuration of **3a** was determined to be *S*,*S* by single crystal X-ray analysis[17] of a tosylated derivative of **3a** (see the Supporting Information).

Table 2: Enantioselective reductive [3+2] cycloaddition of alkynes with cyclic enones.[a]

Entry	1	2	Product 3		Yield [%][b]	*ee* [%]
1	**1a**	**2a**		**3a**: R^1,R^2 = Ph	71	90 (*S*,*S*)
2	**1b**	**2a**		**3b**: R^1,R^2 = 4-MeC_6H_4	64	98
3	**1c**	**2a**		**3c**: R^1,R^2 = 4-ClC_6H_4	54	98
4	**1d**	**2a**		**3d**: R^1,R^2 = 4-BrC_6H_4	61	> 99
5	**1e**	**2a**		**3e**: R^1,R^2 = 2-thienyl	76	77
6	**1g**	**2a**		**3g**: R^2 = Ph	63	90
7	**1i**	**2a**		**3i**: R^2 = naphthyl	50	92
8[c]	**1a**	**2b**		**3l**	69	78
9	**1a**	**2c**		**3n**: R^1 = Ph	54	93
10	**1g**	**2c**		**3o**: R^1 = Me	60	64
11	**1a**	**2d**		**3p**	53	> 99

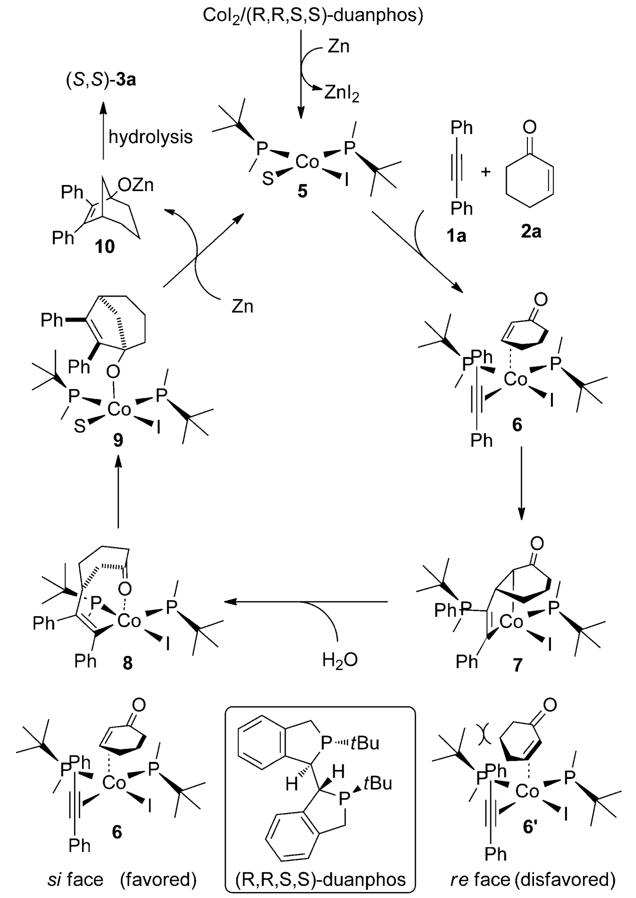
[a] Unless otherwise mentioned, all reactions were carried out using alkyne **1** (0.40 mmol) and alkene **2** (0.60 mmol) in the presence of CoI_2 (5.0 mol%), (*R*,*R*,*S*,*S*)-Duanphos (5.0 mol%), Zn (1.10 mmol), and ZnI_2 (0.20 mmol) in 1,4-dioxane (0.80 mL) at RT for 24 h. [b] Yield of isolated product. [c] Reactions were carried out using CoI_2 (5.0 mol%), (*R*)-binap (5.0 mol%), Zn (1.10 mmol), and $ZnCl_2$ (0.20 mmol) in 1,4-dioxane (0.80 mL) at RT for 24 h.

The CoI_2/(*R*,*R*,*S*,*S*)-Duanphos system was then applied to the asymmetric reductive [3+2] cycloaddition reaction of symmetrical aromatic alkynes, **1b–d**, with **2a**, which provided

3b–d in good yields and with high enantioselectivites (90–99%), (Table 2, entries 2–4). Similarly, **1e** furnished **3e** in 76% yield with a somewhat low *ee* value (77%; entry 5). Unsymmetrical alkynes **1g** and **1i** also underwent cycloaddition with **2a** to give single regioisomeric products **3g** and **3i** in good yields and with 90 and 92% *ee*, respectively (entries 6 and 7).

The scope of the enantioselective cycloaddition reaction was also examined with various cyclic enones, **2b–d** (Table 2, entries 8–11). In contrast to **2a**, 2-cyclopentenone (**2b**) afforded **3l** only in 78% *ee* (entry 8). In the present catalytic asymmetric reaction, it appears that the ring size and the substituent on the cyclic enones significantly affect the *ee* value of the coupling product.[16] For example, 4,4-dimethyl-substituted cyclic enones, **2c** and **2d**, underwent cycloaddition with **1a** to afford products **3n** and **3p** in good yields and with excellent *ee* values (entries 9 and 11). Conversely, a moderate *ee* was observed for **3o** (entry 10). In the present reductive [3+2] cycloaddition reaction of **1** and **2**, a minor amount of corresponding reductive coupling product was obtained in both the racemic and asymmetric variants.

A reaction mechanism that accounts for the absolute configuration of product **3a** is proposed in Scheme 2. The reaction is likely initiated by the reduction of Co$^{\text{II}}$[16,18a–c] to Co$^{\text{I}}$ species **5** by zinc dust. Then, coordination of **1a** in the equatorial position and **2a** with its *si* face in the axial position of the Co$^{\text{I}}$ center to form **6** followed by oxidative cyclization gives cobaltacyclopentene[18d,e] intermediate **7**. Selective protonation[19] at the α-carbon to the keto group of **7** generates **8**. Next, carbonyl insertion into the cobalt-carbon bond forms cobaltalkoxide **9**. Reduction of **9** by Zn dust provides **10** and regenerates the Co$^{\text{I}}$ species. Ultimately, the hydrolysis of **10** in air affords **3a**.



Scheme 2. Proposed mechanism for enantioselective reductive [3+2] cycloaddition of **1a** and **2a**.

The [3+2] cycloaddition is closely related to the corresponding enyne reductive coupling reaction in the mechanistic pathway. Both reactions likely proceed with the same initial steps until the formation of intermediate **8** (Scheme 2). Protonation of **8** at the Co–C bond gives the reductive coupling product **4a**, whereas carbonyl insertion into the Co–C bond of **8** affords product **3a**. As shown in Scheme 2, the absolute configurations of products **3a** and **4a** appear to be determined by the coordination of enone **2a** to the cobalt complex (**6**, *si* face; or **6′**, *re* face). Thus, we anticipate that both reactions using the same chiral ligand should give products with the same absolute configuration and may be the same *ee* values. However, the reaction of **1a** with **2a** in the presence of 2 equivalents of water and a CoI$_2$/(*R*,*R*,*S*,*S*)-Duanphos complex as the catalyst afforded a mixture of reductive coupling product (*S*)-**4**[16] and [3+2] cycloadduct (*S*,*S*)-**3a** in 23 and 41% yield with 54% and 90% *ee*, respectively; whereas, in the absence of extra water (*S*)-**4** and (*S*,*S*)-**3a** were obtained in 7 and 71% yield, with 52% and 90% *ee*, respectively. These results show that the cycloadduct **3a** and the reductive coupling product **4a** have the same absolute configurations, but their *ee* values are quite different. It is noteworthy that intermediate **8** also contains two diastereomers. The ratio of these two diastereomers and their relative reactivity will decide the *ee* values of the products. A possible cause for the *ee* difference is the reactivity difference of the two diastereomers of **8**.

In conclusion, we have demonstrated an atom-economic cobalt-catalyzed reductive [3+2] cycloaddition of alkynes and cyclic enones that affords bicyclic tertiary alcohols with high regioselectivity. Besides, we have also described an asymmetric variant for the synthesis of tertiary alcohols with high *ee* values (up to 99% *ee*). This catalytic reaction proceeds with high regio- and stereoselectivity. In the reaction, an air-stable, relatively inexpensive cobalt catalyst, a mild reducing agent, Zn, and one of the simplest hydrogen sources, water, were used.

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[19] We believe that a trace amount of water present in the solvent may lead to the protonation of intermediate **7**.