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Title	Cobalt(I)-Catalyzed Reductive Cyclization of Enynes and Diynes Using Hydrogen Gas as a Reductant
Author(s)	Isoda, Kaho; Sato, Yoshihiro
Citation	Organic letters, 25(12), 2103-2107 https://doi.org/10.1021/acs.orglett.3c00524
Issue Date	2023-03-31
Doc URL	https://hdl.handle.net/2115/91879
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Type	journal article
File Information	OL_Isoda.pdf

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Cobalt(I)-Catalyzed Reductive Cyclization of Enynes and Diynes Using Hydrogen Gas as a Reductant

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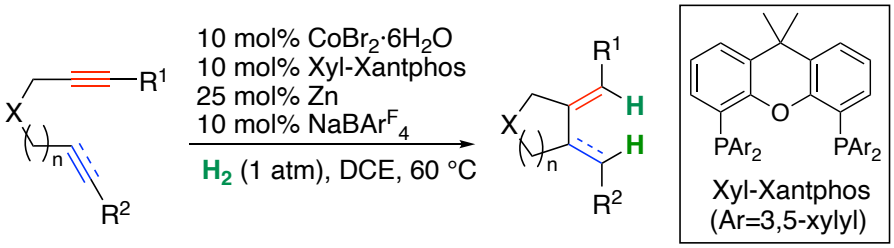
Supporting Information Placeholder

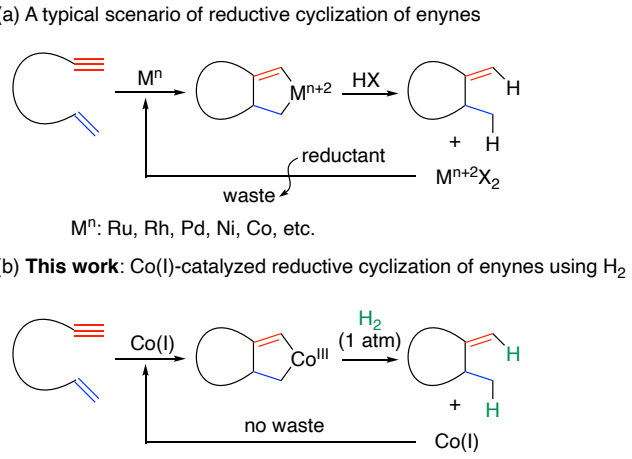


ABSTRACT: Reductive cyclization of enynes and diynes by using H_2 gas as a reductant was realized, and the corresponding cyclized products were obtained in good yields without olefin-isomerization and over-reduction of the products. By an experiment using D_2 instead of H_2, it was confirmed that H_2 unambiguously operates as a reductant in this reaction. The protocol of the reaction is very economical and user-friendly by using air- and moisture-stable $CoBr_2 \cdot 6H_2O$ and 1 atm pressure of H_2.

Reductive coupling between two different π components (e.g., alkenes, alkynes, and carbonyl groups) is one of the unique reactions catalyzed by transition metal catalysts.[1] Reductive cyclization between diynes or an alkyne and an alkene is a promising methodology for regio- and stereoselective construction of cyclic compounds. Most of the reactions proceed via a metallacycle intermediate formed through oxidative cycloaddition of C-C multiple bonds to a low valent metal complex (M^n), and it is known that various transition metals such as Pd,[2] Ni,[3,4] and Co[3c,5] can catalyze this type of reaction (Scheme 1). As a typical scenario of reductive cyclization of enynes shown in Scheme 1 (a), cleavage of the C-M bond in the metallacycle occurs by a hydrogen source (e.g., HX), giving a cyclized product along with formation of $M^{n+2}X_2$. To establish a catalytic cycle of this reaction, more than a stoichiometric amount of a reductant is necessary to reduce $M^{n+2}X_2$ to M^n. Thus, more than a stoichiometric amount of waste originating from the reductant is also produced after the reaction, and that is a serious drawback of this reaction.

Hydrogen gas (H_2) is one of the ideal reductants in various transformations including the above-mentioned reductive couplings because it is cheap and easily accessible and there is no production of waste after the reaction. Furthermore, with increasing utilization of H_2 in various fields, technology for production of H_2 without CO_2 emission is being developed to replace the traditional methods such as steam reforming.[6] However, the utilization of H_2 as a reductant in transition metal-catalyzed C-C-bond forming reactions has been limited, probably due to competition with catalytic hydrogenation. In 2002, Krische and coworkers reported Rh-catalyzed reductive coupling between an enone and an aldehyde with H_2 (1 atm).[7] After that, they showed that H_2 can be used as a reductant in various types of reductive coupling, including reductive cyclization of enynes,[8] in a series of their excellent studies.[9] However, reductive cyclizations of enynes or diynes using H_2 as a reductant have been limited, and there have been only a few reports so far.[10] We herein report Co(I)-catalyzed reductive cyclization of enynes and diynes by using 1 atm of H_2 as a reductant (Scheme 1 (b)).[11]

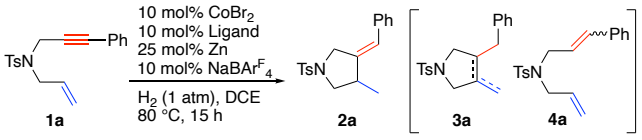
Scheme 1. Transition Metal-Catalyzed Reductive Cyclization of Enynes



Initially, the reaction of enyne **1a** with 10 mol% of the cationic Co(I) catalyst, prepared in situ from $CoBr_2$ (10 mol%) and various ligands in the presence of Zn (25 mol%) and $NaBAr^F_4$ (10 mol%) in a manner similar to the reported procedure,[5a] was carried out in dichloroethane (DCE) at 80 °C under 1 atm of H_2, and the results are

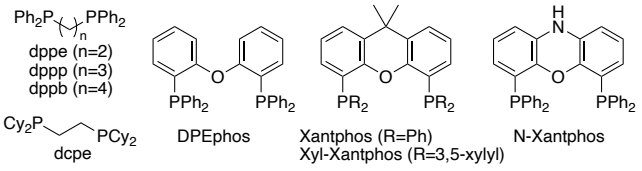
summarized in Table 1. The use of monodentate ligands, PPh_3 and PCy_3, was not effective for producing the desired compound **2a**, and most of **1a** was recovered in each reaction (Entries 1 and 2). Co(I) catalysts bearing bidentate ligands such as dppe, dppp, dppb, dcpe, and DPEphos promoted the cyclization, but a large amounts of isomerized product **3a** and/or alkyne-reduced starting material **4a** were obtained along with desired product **2a** (Entries 3-7). On the other hand, it was found that Xantphos-type ligands were effective for selective formation of the desired product **2a** without isomerized product **3a**. Thus, reactions of **1a** using Xantphos, N-Xantphos, and Xyl-Xantphos gave **2a** in 68%, 75%, and 83% yields, respectively, with a small amount of the reduced starting material **4a** (Entries 8-10).

Table 1. Ligand Screening in Reaction of 1a[a]



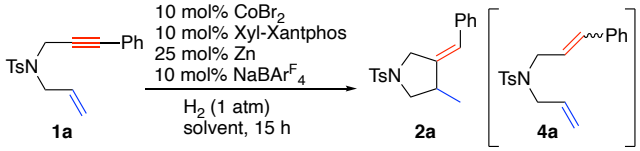
Entry	Ligand	**2a** (%)	**3a** (%)	**4a** (%)	Recov. **1a** (%)
1[b,c]	PPh_3	–	–	trace	87
2[d]	PCy_3	–	–	–	quant.
3	dppe	23	17	5	5
4	dppp	21	44	trace	–
5	dppb	27	46	–	–
6	dcpe	48	33	–	–
7	DPEPhos	17	34	3	–
8	Xantphos	68	–	7	–
9	N-Xantphos	75	–	1	–
10	Xyl-Xantphos	83	–	6	–

[a]Unless noted otherwise, the yields are isolated ones. [b]The yield was determined by ^{1}H-NMR analysis with 1,1,2,2-tetrachloroethane as an internal standard. [c]10 mol% of $CoBr_2(PPh_3)_2$ was used. [d]20 mol% of PCy_3 was used.



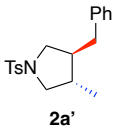
Next, we commenced further optimization of the reaction conditions in the reaction of **1a** using Xyl-Xantphos as a ligand (Table 2). When the reaction temperature was lowered from 80 °C to 60 °C, the yield was not affected, and the cyclized product **2a** was obtained in 82% yield (entry 1). On the other hand, in the reaction at 40 °C, the yield of **2a** was decreased to 52%, and over-reduced product **2a'** was also obtained in 15% yield, although the reason was not clear (Entry 2). For solvents, the reaction in toluene at 60 °C produced **2a** in 76% yield, while the use of THF and CH_3CN at the same temperature decreased the yield of **2a** to 36% and 4%, respectively (Entries 3-5). In these reactions, we used a cationic Co(I) catalyst formed in situ from $CoBr_2$ (10 mol%) and various ligands in the presence of Zn (25 mol%) and $NaBAr^F_4$ (10 mol%). When the amount of Zn was decreased from 2 to 10 mol%, the time required for complete consumption of the substrate **1a** was extended to 39 hours, but **2a** was obtained in good yield (Entry 6). On the other hand, the reaction in the absence of Zn or $NaBAr^F_4$ did not proceed at all, and the starting material **1a** was almost completely recovered (Entries 7 and 8), meaning that these reagents are necessary for formation of the active Co catalyst. It is noteworthy that the reaction under an atmosphere of N_2 instead of H_2 also did not proceed, indicating that H_2 plays a critical role for the reaction to proceed (Entry 9).

Table 2. Optimization for Reductive Cyclization of 1a[a]



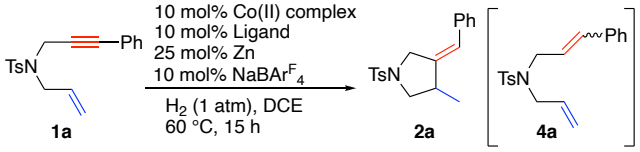
Entry	conditions	**2a** (%)	**4a** (%)	Recov. **1a** (%)
1	DCE, 60 °C	82	6	–
2[b]	DCE, 40 °C	52	3	–
3	toluene, 60 °C	76	8	–
4	THF, 60 °C	36	59	–
5	CH_3CN, 60 °C	4	trace	22
6[c]	10 mol% Zn	79	3	–
7[d]	w/o Zn	–	–	95
8[d]	w/o $NaBAr^F_4$	–	–	98
9[d]	w/o H_2 (under N_2)	–	–	94

[a]Unless noted otherwise, the yields are isolated ones. [b]**2a'** was obtained in 15% yield. [c]Reaction time was 39 h. [d]The yield was determined by ^{1}H-NMR analysis with 1,1,2,2-tetrachloroethane as an internal standard.



In all of the experiments shown in Tables 1 and 2, commercially available "anhydrous $CoBr_2$" was used as received. Since anhydrous $CoBr_2$ is known to be hygroscopic, we decided to use it after drying by heating at 130 °C *in vacuo* for 24 hours. As a result, in the reaction of **1a** with dried $CoBr_2$ (10 mol%) and Xantphos (10 mol%), the yield of **2a** significantly decreased to 20%, and the starting material **1a** was recovered in 80% yield (Table 3, Entry 1). With the addition of 20 mol% water to the reaction under the same conditions, the yield of **2a** was slightly improved to 36% (Entry 2). Surprisingly, the use of $CoBr_2{\cdot}6H_2O$, which is the most stable hydrate complex of $CoBr_2$, increased the yield of **2a** to 90% (Entry 3). With the use of a Co(I) catalyst under the same conditions with Xyl-Xantphos, the yield of **2a** reached 95% (Entry 4). Furthermore, in the reaction of 1 mmol scale of **1a**, catalyst loading can be reduced to 2 mol%, and the product **2a** was obtained in a high yield (Entry 5). As for the reason why $CoBr_2{\cdot}6H_2O$ was more effective than "anhydrous" or dried $CoBr_2$, we speculate that the presence of H_2O promoted the reduction of Co(II) species to Co(I) species by zinc. Similarly, Chirik recently reported that the presence of MeOH accelerated the reduction of a Co(II)-diphosphine complex to Co(I)-diphosphine complex by zinc as a reductant.[12]

Table 3. Optimization for Preparation of a Co(I) Catalyst[a]

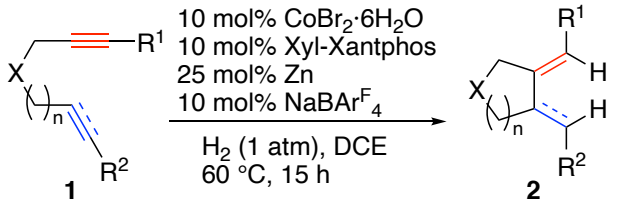


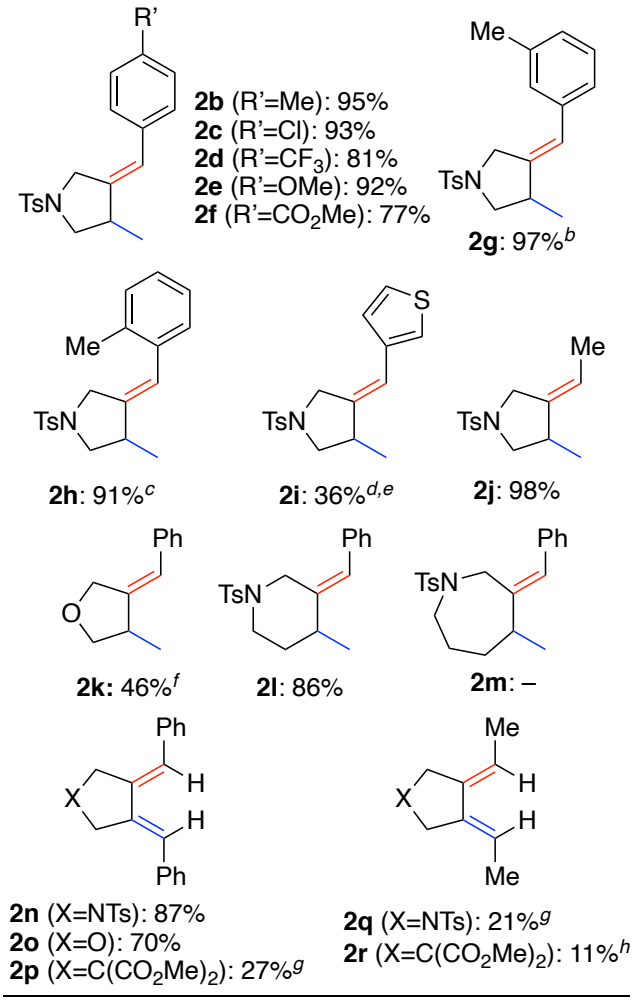
Entry	Co(II) complex	2a (%)	4a (%)	Recov. **1a** (%)
1[b,c]	$CoBr_2$ (dried)	20	–	80
2[c]	$CoBr_2$ (dried)+20 mol% H_2O	36	6	–
3[c]	$CoBr_2 \cdot 6H_2O$	90	10	trace
4[d]	$CoBr_2 \cdot 6H_2O$	95	4	–
5[e]	2 mol% $CoBr_2 \cdot 6H_2O$	85	5	–

[a]Unless noted otherwise, the yields are isolated ones. [b]The yield was determined by ^{1}H-NMR analysis with 1,1,2,2-tetrachloroethane as an internal standard. [c]Xantphos was used as a ligand. [d]Xyl-Xantphos was used as a ligand. [e]1 mmol of **1a**, Xyl-Xantphos (2 mol%), Zn (5 mol%), and NaBAr$^F_4$ (2 mol%) were used in this reaction.

With the optimal conditions in hand, we next investigated the scope of substrates in this cyclization (Table 4). Various substituents, including electron-donating and electron-withdrawing groups, at the *p*-position of the aromatic ring at the terminus of the alkyne of enynes **1** were tolerated to give the corresponding cyclized products **2b**-**2f** in 77%-95% yields. The reaction of **1g** having a methyl group at the *m*-position of the aromatic ring took 24 hours to complete, but the desired product **2g** was obtained in an excellent yield (97%). On the other hand, the reaction of **1h** having a methyl group at the *o*-position did not proceed under the optimal conditions, probably due to the steric repulsion. In this case, however, the use of Xantphos instead of Xyl-Xantphos was effective and the product **2h** was obtained in 91% yield. The existence of a heteroaromatic ring, thiophene, at the terminus of the alkyne somewhat retarded the reaction, but the cyclized product **2i** was obtained in a modest yield (36%). The reaction of **1j** having a methyl group at the terminus of the alkyne gave **2j** in 98% yield, indicating that the existence of an aromatic ring at the alkyne terminus is not essential. The presence of oxygen in the chain is also tolerated, but the yield of **2k** was diminished to 46%. With respect to substrates having longer chains, the reaction of 1,7-enyne **1l** gave the desired product **2l** in 86% yield, while the reaction of 1,8-enyne **1m** did not proceed, recovering **1m** in 87% NMR yield. Next, the reaction of 1,6-diynes were checked under the same conditions. In the case of 1,6-diyne **1n** having a Ts amide moiety and phenyl substituents at each terminus of alkynes, the corresponding product **2n** was obtained in 87% yield. Changing the Ts amide moiety in **1n** to oxygen did not affect the yield of the product, giving **2o** in 70% yield. On the other hand, the malonate derivative **1p** did not seem to be a good substrate in this reaction, giving the corresponding product **2p** in 27% yield. Compared to diynes having phenyl substituents on the alkynes, 1,6-diynes **1q** and **1r** having methyl substituents on the alkynes are not suitable for this reaction, and the corresponding products **2q** and **2r** were obtained in 21% and 11% yields, respectively. Although it is a preliminary result, it is noteworthy that the reaction of allenyne **5** under the optimal conditions gave the product **6** in an excellent yield (99%)(Scheme 2).

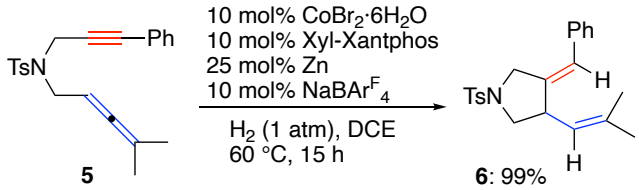
Table 4. Scope of Substrates[a]





[a]Isolated yields. [b]The reaction time was 24 h. [c]10 mol% of Xantphos was used instead of Xyl-Xantphos. [d]The reaction time was 48 h. [e]The reduced starting material **4i** was also obtained in 27% yield. [f]The residual starting material **1k** was observed as the mixture with unidentified byproducts. [g]The starting material was almost consumed, and unidentified byproducts were also formed. [h]Most of the starting material remained but could not be separated from unidentified byproducts.

Scheme 2. Reaction of Allenyne[a]



[a]Isolated yields.

To gain an insight into the reaction mechanism, we conducted the reaction of **1a** under the optimal conditions using deuterium gas (D_2) instead of H_2 (Figure 1, upper part). As a result, the product **2a**-*d* was obtained in 87% yield, with deuterium being incorporated at each of the expected positions in **2a**-*d* with high D-contents (>95%). This result indicates that H_2 (or D_2) unambiguously acts as a reductant in the reaction. Also, it means that H_2O in $CoBr_2{\cdot}6H_2O$ and a catalytic amount of Zn (25 mol%) do not operate as reductants for the cyclization, and those would be necessary for preparation of an active Co(I) catalyst from a Co(II) complex.

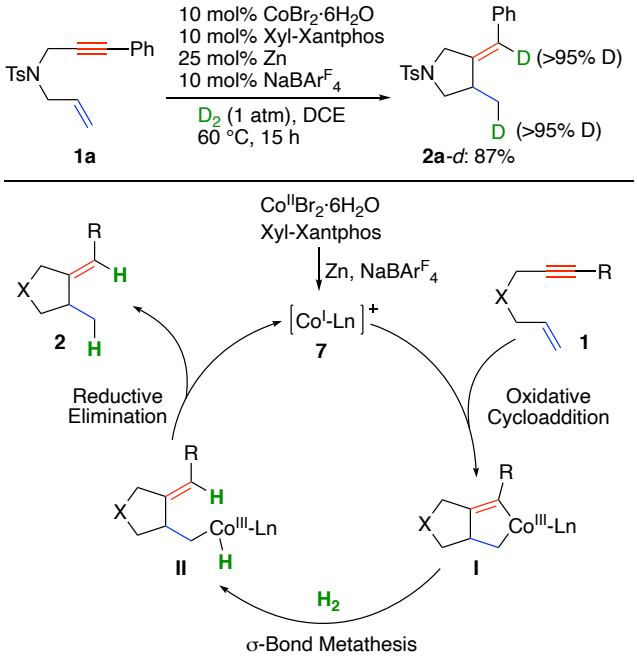


Figure 1. Reaction using D_2 and Proposed Mechanism

Based on the above-described result, the proposed mechanism of this reductive cyclization is shown in the lower part of Figure 1. A cationic Co(I) catalyst **7** was formed by reduction of $CoBr_2{\cdot}6H_2O$ by Zn in the presence of a ligand and $NaBAr^F{}_4$. Oxidative addition of substrate **1** to Co(I) catalyst **7** produced cobaltacycle intermediate **I**, which is the common intermediate in reductive cyclization catalyzed by a transition metal catalyst.[1-6] Then, σ-bond metathesis between **I** and H_2 occurred to give intermediate **II**,[13,14] from which reductive elimination afforded product **2** along with regeneration of Co(I) catalyst **7**. We speculate that a Xantphos-type ligand operates as a tridentate ligand in this reaction, which results in the prevention of side reactions such as isomerization and over-reduction by occupation of three coordination sites on the cobalt center.[15]

In conclusion, we succeeded in developing Co(I)-catalyzed reductive cyclization of enynes and diynes using H_2 as a reductant. The remarkable features of this reaction are as follows: (1) The reaction is economical and convenient owing to the use of the base metal Co and easily accessible H_2 and (2) the experimental protocol is user-friendly with easy handling owing to the use of an air-and moisture-stable $CoBr_2{\cdot}6H_2O$ complex under 1 atm pressure of H_2. Further studies including extension to an asymmetric variant are in progress.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its online Supporting Information.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details and spectral data of substrate, cyclized product, and copies of NMR of the key compounds (PDF).

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was financially supported in part by Grant-in-Aid for Scientific Research (B) (No. 20H03360) from the Japan Society for the Promotion of Science. This work was also partly supported by Hokkaido University, Global Facility Center (GFC), Pharma Science Open Unit (PSOU), funded by MEXT under "Support Program for Implementation of New Equipment Sharing System".

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