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Letter

$Ru_3(CO)_{12}$-Catalyzed Reaction of 1,6-Diynes, Carbon Monoxide, and Water via the Reductive Coupling of Carbon Monoxide

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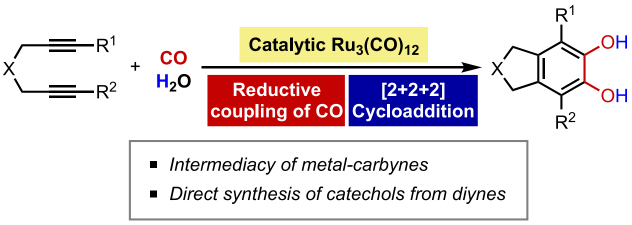
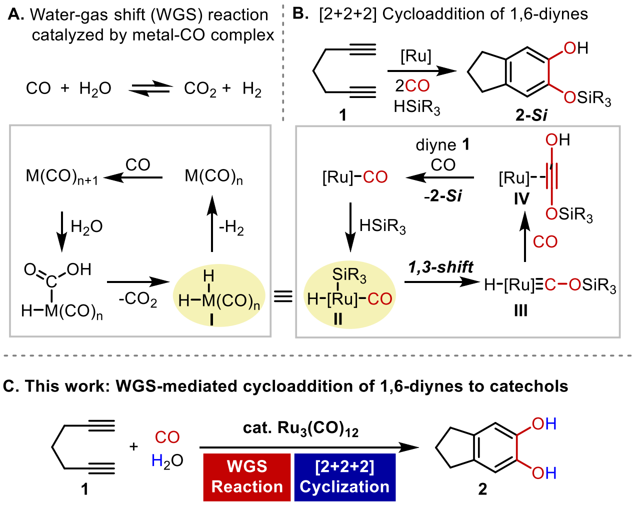
ABSTRACT: We report the ruthenium-catalyzed cyclization of 1,6-diynes with two molecules of carbon monoxide and water to give a variety of catechols. This reaction likely proceeds through the intermediacy of the water−gas shift reaction to generate an yne−diol-type intermediate followed by a [4 + 2] cycloaddition with 1,6-diynes. The reaction requires no external reductants or hydride sources and provides a novel and valuable method for the synthesis of a variety of catechols.



- *Intermediacy of metal-carbynes*
- *Direct synthesis of catechols from diynes*

The water−gas shift (WGS) reaction is a crucial industrial process for the production of high purity hydrogen gas from carbon monoxide (CO) and water. Metal dihydrides (**I**) are key intermediates (Scheme 1A).[1] The WGS reaction has been also applied in hydrogenation reactions as well as catalytic reactions for the regeneration of active catalytic species;[2] however, its use in organic synthesis remains underdeveloped.

Scheme 1. Water−Gas Shift Reaction for the Synthesis of Catechols from 1,6-Diynes



Our group previously reported that 1,6-diynes react with carbon monoxide and hydrosilane in the presence of simple Ru catalysts to provide catechol derivatives (Scheme 1B).[3] This reaction is proposed to proceed via a unique 1,3-shift of the silyl group in complex **II** to the oxygen atom of a coordinated CO.[4] Reaction of the resulting silyloxycarbyne complex **III** with a second molecule of CO gives dioxyacetylene **IV**.[5] This species can be trapped by cycloaddition with diynes **1**,[6] yielding monosilylated catechols **2**-*Si* (Scheme 1B). We speculated that this reaction might be carried out under WGS conditions if metal dihydride **I** could be considered a surrogate for **II**.

The use of metal catalysts to affect the cycloaddition of alkynes and diynes with a variety of partners, including other alkynes, alkenes, carbon dioxide, and nitriles, has become a topic of intense interest.[7] However, the synthesis of catechols through this type of cycloaddition has not been reported, even though early transition metals have been shown to affect the reductive coupling of CO to yield disiloxyethylenes under stoichiometric conditions.[8] Other examples where two molecules of CO are incorporated result in the preparation of 1,4-benzoquinones or 1,4-hydroquinones and thus do not proceed through the intermediacy of dihydroxyethyne.[9] Interestingly, despite their well-documented use in metathesis reactions and stoichiometric organometallic chemistry,[10a,b] metal carbyne species are scarcely invoked in catalytic transformations.[10c,d]

Herein, we report a novel, scalable synthesis of catechols through the intermediacy of a WGS reaction, where water is employed as the source of hydrogen, via metal carbynes as likely intermediates (Scheme 1C).

To optimize the reaction, we began with substrate **1a**, which is predisposed toward cyclization because of the Thorpe−

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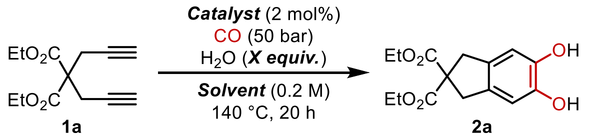
Ingold effect introduced by the geminal ester substituents. Reaction between **1a** and carbon monoxide was carried out in a stainless steel autoclave employing 50 atm of CO and a polar solvent to which several equivalents of water was added. $Ru_3(CO)_{12}$ was employed as the catalyst at 2 mol % loading and the reaction carried out at 140 °C for 20 h. Under these conditions, the desired product (**2a**) was isolated after trituration in 81% yield (Table 1, entry 1).

Table 1. Optimization of Reaction Conditions for Cycloaddition of 1,6-Diyne 1a



entry	catalyst	H_2O (equiv)	solvent	yield (%)
1	$Ru_3(CO)_{12}$	4	1,4-dioxane	81
2	$Ru_3(CO)_{12}$	5	1,4-dioxane	70
3	$Ru_3(CO)_{12}$	2	1,4-dioxane	51
4[a]	$Ru_3(CO)_{12}$	4	1,4-dioxane	61
5[b]	$Ru_3(CO)_{12}$	4	1,4-dioxane	24
6	$Fe_3(CO)_{12}$	4	1,4-dioxane	0
7	$Os_3(CO)_{12}$	4	1,4-dioxane	0
8	$Ru_3(CO)_{12}$	4	CH_3CN	79
9	$Ru_3(CO)_{12}$	4	THF	81
10	$Ru_3(CO)_{12}$	4	CH_2Cl_2	46
11	$Ru_3(CO)_{12}$	4	toluene	38
12	$Ru_3(CO)_{12}$	4	CH_3OH	51

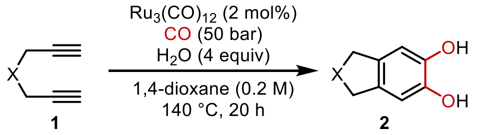
[a] CO pressure: 30 bar. [b] Reaction temperature:120 °C.

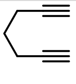
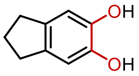
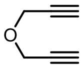
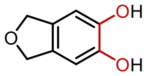
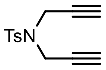
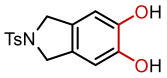
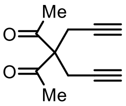
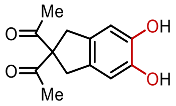
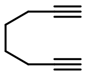
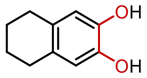
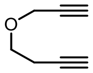
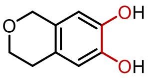
Using larger or smaller amounts of water gave decreased yields of product **2a** (70% yield for 15 mmol of H_2O and 51% yield for 6 mmol of H_2O, entries 2 and 3). Decreasing the CO pressure also led to lower product yields (30 atm of CO gave 61% yield) as did lower temperatures (24% yield at 120 °C) (entries 4 and 5). Using $Fe_3(CO)_{12}$ or $Os_3(CO)_{12}$ as the catalyst in place of $Ru_3(CO)_{12}$ gave no reaction (entries 6 and 7). The reaction was tolerant to other solvents such as CH_3CN (79%) and THF (81%); however, lower yields were obtained in CH_2Cl_2 (46%), toluene (38%), and CH_3OH (51%) (entries 8−12).

These optimized conditions (Table 1, entry 1) were then applied to a variety of diyne substrates (Table 2). Gratifyingly, the cycloaddition reaction did not require geminal substitution on the diyne, with the simple 1,6-heptadiyne (**1b**) reacting to give catechol **2b** in 59% yield. Oxygen or nitrogen substitution in the tether as in **1c** and **1d** were well tolerated as was the ketone in **1e**, yielding catechols **2c**−**2e**. However, 1,7-heptadiyne (**1f**), which would yield the tetrahydronaphthalene structure, gave a complex mixture of products as did the related ether **1g**, illustrating the importance of the fused 5/6 ring.

Internal alkynes could also be employed as shown in Table 3. Diynes bearing a single substituent at the acetylenic terminus (methyl, **1h**, or phenyl, **1j**) gave adducts **2h** and **2j** in good yields, although terminal ethyl ester-substituted diyne **1i** reacted with much lower efficiency. Disubstituted diynes **1k** and **1l** reacted smoothly to afford the corresponding hexasubstituted catechols **2k** and **2l**; however, diphenyl derivative **1m** gave none of the desired product.

Table 2. Reaction of Terminal Alkynes with CO and H_2O in the Presence of $Ru_3(CO)_{12}$[a]



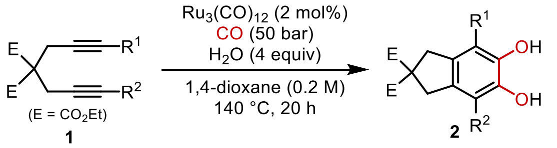
entry	diyne **1**	product **2**	yield (%)
1	 **1b**	 **2b**	59
2	 **1c**	 **2c**	66
3	 **1d**	 **2d**	43
4	 **1e**	 **2e**	76
5	 **1f**	 **2f**	0
6	 **1g**	 **2g**	0

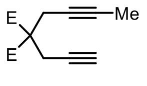
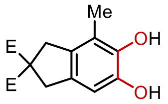
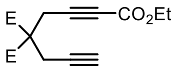
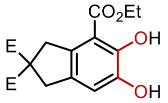
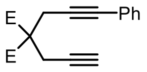
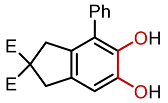
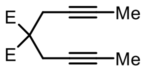
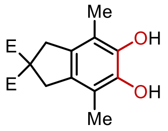
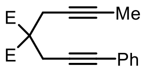
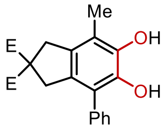
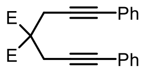
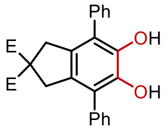
[a] Yields reported for isolated products.

Although identifiable byproducts were rarely observed, a side product from the reaction of diphenyl diyne **1m** was instructive. Instead of the desired catechol, cyclopentadieneone−Ru complex **3m** was isolated. This species results from incorporation of a single molecule of carbon monoxide in a well-precedented [2 + 2 + 1] cycloaddition, with $Ru(CO)_3$ binding to the cyclopentadieneone unit.[11] This compound was isolated in 89% yield relative to the added ruthenium catalyst (Scheme 2), and its structure was confirmed spectroscopically and by X-ray crystallography (Figure 1). The observation of compound **3m** suggests that the [2 + 2 + 1] cycloaddition reaction is less sensitive to steric constraints than the desired [2 + 2 + 2] and that, once formed, these adducts can serve as catalyst sinks halting further transformations. Previous studies of Ru-catalyzed cycloadditions of diynes have documented the observation of related compounds, especially with sterically hindered diynes.[12]

The catechol synthesis was also attempted employing alkyne **1n**, which contains a terminal nitrile, since a successful cycloaddition would yield a pyridone product. Unfortunately, conditions were not found to affect pyridone synthesis, although product **2n** was observed in small amounts along with other unidentified products (Scheme 3). Since catechol

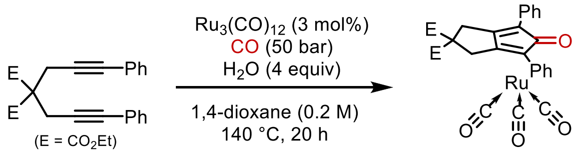
Table 3. Reaction of Internal Alkynes with CO and H_2O in the Presence of $Ru_3(CO)_{12}$[a]



entry	diyne **1**	product **2**	yield (%)
1	 **1h**	 **2h**	76
2	 **1i**	 **2i**	12(18)[b]
3	 **1j**	 **2j**	64[b]
4	 **1k**	 **2k**	75
5	 **1l**	 **2l**	47(57)[b]
6	 **1m**	 **2m**	0

[a]Yields reported for isolated products. ^1H NMR yields are shown in parentheses (1,3,5-trimethoxybenzene was used as an internal standard). [b]With 6 mol % of $Ru_3(CO)_{12}$.

Scheme 2. Reaction of Diphenyl Diyne



3m, 22% isolated yield (89% ^1H NMR yield)

2n was presumably produced by an unprecedented *inter*-molecular cycloaddition, we also examined the reaction of phenyl acetylene; however, none of the desired product was observed from this alkyne.

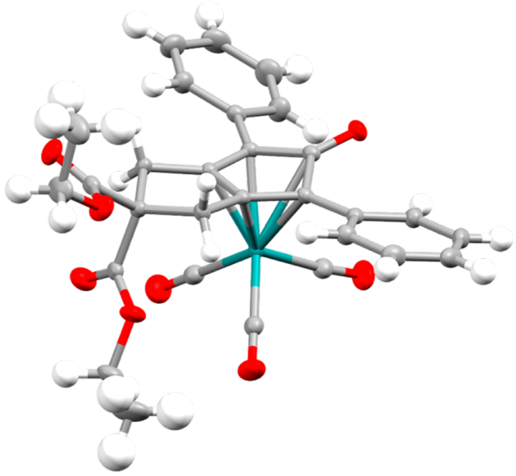
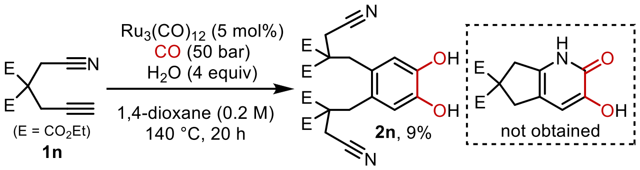
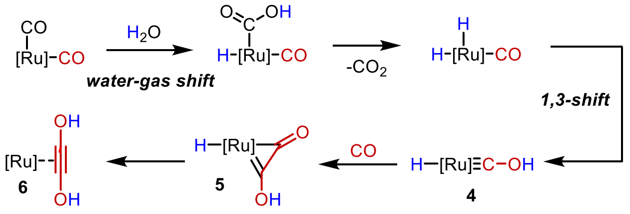


Figure 1. Single-crystal X-ray structure of compound **3m** (Ru, green; C, gray; O, red). Thermal elipsoids are shown at 50% probability. Selected bond lengths (Å) and angles [degs]: avg Ru−C$_{(C\equiv O)}$ = 1.936(2); avg C−O$_{(C\equiv O)}$ = 1.130(2); avg C$_{(C\equiv O)}$−Ru−C$_{(C\equiv O)}$ = 94.86(7).

Scheme 3. Reaction of Alkyne Bearing a Terminal Nitrile



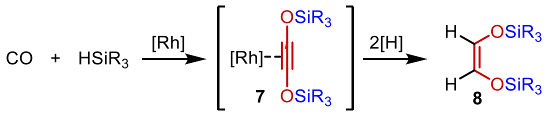
Scheme 4. Proposed Reaction Pathway



From a mechanistic point of view, the use of water in place of hydrosilane is somewhat remarkable since these two reagents are at different oxidation states. As noted in the introduction, the most reasonable suggestion for the observed product is that metal hydrides are generated in situ via the water gas shift reaction (Scheme 4).[1] Isomerization of the proposed intermediate metal carbonyl dihydride via a 1,3-metal hydride shift gives hydroxycarbyne metal complex **4**. The suggested 1,3-hydride shift (Scheme 4) is proposed on the basis of precedent from related silyl systems[4] and considerable other literature describing the intermediacy of hydroxy carbynes such as **4** as an alternative to the less stable formyl tautomers.[13] Reaction of this species with another molecule of carbon monoxide would result in yne−-diol metal complex **6** via a metallacyclopropenone **5** in analogy with similar reactivity seen in other metal complexes.[5,14]

The feasibility of yne−diol complex **6** is supported by reactions of related hydrosilanes performed in the absence of the 1,6-diyne (Scheme 5).[15] We previously reported that the Rh-catalyzed reaction between CO and a hydrosilane gives ene−diol **8**, presumably derived from metal ene-silanol derivative **7**. The stereochemistry of the ene-silanol **8** was shown to be *cis*, as expected for the mechanism shown.

Scheme 5. Formation of Ene–Diol in the Absence of Diene



In conclusion, we have developed a ruthenium-catalyzed catechol synthesis from a variety of diynes utilizing the WGS reaction to generate 1,2-hydroxyethyne from two molecules of CO and water. Reactions proceeding via metal carbyne complexes remain under represented in catalytic transformations. In this context, it is noteworthy that formation of a metal oxy–acetylene complex from a metal carbyne, carbon monoxide, and hydrogen is a likely pathway for the transformations described. Efforts to expand the synthetic applicability of this unique reactive intermediate are in progress.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02349.

Experimental details and NMR spectra (PDF)

Accession Codes

CCDC 2010656 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(2) For selected recent reports using the WGS reaction for transformations of organic molecules, see: (a) Beucher, H.; Merino, E.; Genoux, A.; Fox, T.; Nevado, C. κ^3-(N^C^C)Gold(III) Carboxylates: Evidence for Decarbonylation Processes. *Angew. Chem., Int. Ed.* **2019**, *58*, 9064–9067. (b) Kolesnikov, P. N.; Usanov, D. L.; Muratov, K. M.; Chusov, D. Dichotomy of Atom-Economical Hydrogen-Free Reductive Amidation vs Exhaustive Reductive Amination. *Org. Lett.* **2017**, *19*, 5657–5660. (c) Zhou, P.; Yu, C.; Jiang, L.; Lv, K.; Zhang, Z. One-pot reductive amination of carbonyl compounds with nitro compounds with CO/H_2O as the hydrogen donor over non-noble cobalt catalyst. *J. Catal.* **2017**, *352*, 264–273. (d) Ibrahim, M. Y. S.; Denmark, S. E. Palladium/Rhodium Cooperative Catalysis for the Production of Aryl Aldehydes and Their Deuterated Analogues Using the Water-Gas Shift Reaction. *Angew. Chem., Int. Ed.* **2018**, *57*, 10362–10367.

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