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Ruthenium-Catalyzed Reaction of 1,6-Diynes with Hydrosilanes and Carbon Monoxide: A Third Way of Incorporating CO

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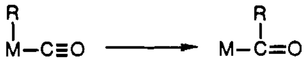
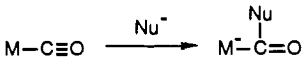
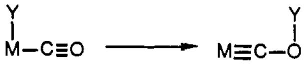
Transition-metal-catalyzed carbonylation has been a powerful tool for preparation of a variety of carbonyl compounds.[1] All these catalytic processes involve either of two distinct mechanisms as the key step: (1) migration of an R group from a metal to the coordinated CO (eq 1) or (2) nucleophilic attack on the coordinated CO by an external nucleophile (eq 2).[2] We now report a new ruthenium-catalyzed reaction of 1,6-diynes with $HSiR_3$ and CO leading to catechol derivatives (vide infra, eq 4),[3] the catalytic cycle of which involves a third way of incorporating CO via an oxycarbyne complex (eq 3). In addition, the new transformation is unique in that it represents a rare example of catalytic incorporation of CO into a diyne[4] and also it exhibits a new mode of successive incorporation of two molecules of CO.[5]



$$\overset{R}{\overset{|}{M}}-C\equiv O \longrightarrow M-\overset{R}{\overset{|}{C}}=O \qquad (1)$$



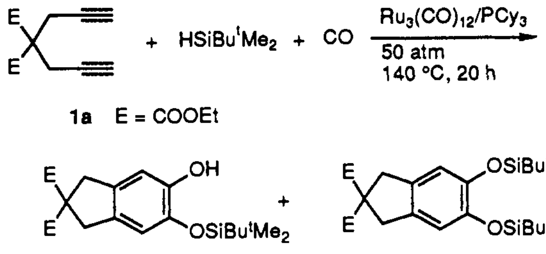
$$M-C\equiv O \xrightarrow{Nu^-} M^{-}-\overset{Nu}{\overset{|}{C}}=O \qquad (2)$$



$$\overset{Y}{\overset{|}{M}}-C\equiv O \longrightarrow M\equiv C-\overset{Y}{\overset{|}{O}} \qquad (3)$$

Y = H, $SiMe_3$

The ruthenium carbonyl/phosphine catalyzed reaction of 1,6-diyne **1a** with $HSiBu^tMe_2$[6] and CO gave two catechol derivatives, 5-(*tert*-butyldimethylsiloxy)-1,3-dihydro-6-hydroxy-2*H*-indene-2,2-dicarboxylic acid diethyl ester (**2a**) and 5,6-bis(*tert*-butyldimethylsiloxy)-1,3-dihydro-2*H*-indene-2,2-dicarboxylic acid diethyl ester (**3a**),[7] or in certain cases afforded only one of these (eq 4). Selected results are given in Table I. Obviously, **2a** is the primary product and it gives **3a** by further silylation. A rationale for the formation of **2a** is shown in Scheme I. Many precedents in stoichiometric reactions strongly suggest that the steps from a carbyne complex **5** to the product **2** are quite reasonable. A carbyne[8]/CO coupling (similar to steps from **5** to an oxyacetylene complex via **6**) has been well studied for tungsten.[9] Complexes of bis(siloxy)acetylene with Nb,[10 a,b] Ta,[10a,b] V,[10c] and Mn[10d] similar to **7** (but without a diyne moiety) are known.



1a

2a

3a

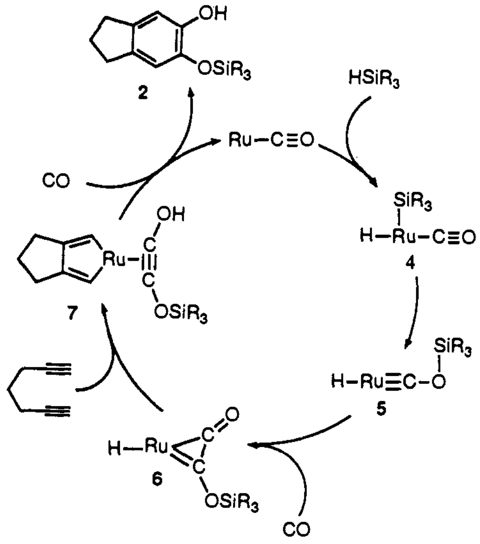
(4)

Table I. Ruthenium-Catalyzed Reaction of **1a** with $HSiBu^tMe_2$ and CO[a]

run	**1a**, mmol	$HSiBu^tMe_2$, mmol	solvent	product[b]	
				2a, %	**3a**, %
1	1	3	dioxane	52	0
2	1	3	toluene	34	0
3	1	3	CH_3CN	40	31
4	1	6	CH_3CN	0	74
5[c]	1	6	CH_3CN	0	60

[a] Reaction conditions: $Ru_3(CO)_{12}$ (0.02 mmol), PCy_3 (0.06 mmol), CO (50 atm), solvent (10 mL) at 140 °C for 20 h. [b] Isolated yields. [c] No tricyclohexylphosphine was added.

Scheme I



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[5] For a review on so-called "double carbonylation", see: Collin, J. *Bull. Soc. Chim. Fr.* **1988**, *6*, 976. See also ref 1.

[6] Because of product stability $HSiBu^tMe_2$ was used throughout this work although other trialkylsilanes reacted similarly.

[7] Typically: In a 50-mL stainless steel autoclave were placed **1a** (236 mg, 1 mmol), $HSiBu^tMe_2$ (1.0 mL, 6 mmol), $Ru_3(CO)_{12}$ (12.6 mg, 0.02 mmol), PCy_3 (16.8 mg, 0.06 mmol), and CH_3CN (10 mL). The reaction mixture was then charged with CO to 50 atm at 25 °C and heated at 140 °C for 20 h. The solvent was removed in vacuo, and the product was isolated by column chromatography on silica gel (hexane/EtOAc = 20/1, 387 mg, 74%). All new compounds were adequately characterized, see the supplementary material.

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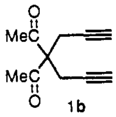
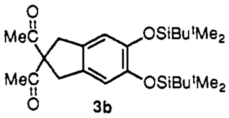
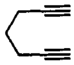
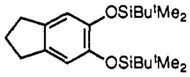
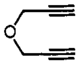
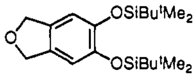
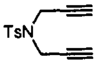
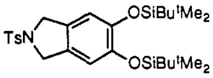
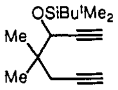
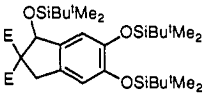
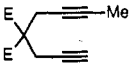
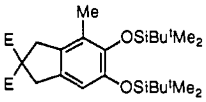
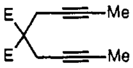
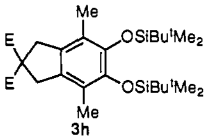
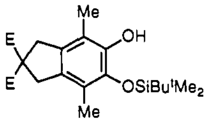
Table II. Ruthenium-Catalyzed Reaction of Diynes with $HSiBu^tMe_2$ and CO Leading to Catechols[a]

entry	diyne	product	yield[b]
1	 1b	 3b	71
2	 1c	 3c	45
3	 1d	 3d	40
4	 1e	 3e	45
5	 1f	 3f	73
6	 1g	 3g	62
7	 1h	 3h	53
		 2h	6

[a] Reaction conditions: diyne (1 mmol), $HSiBu^tMe_2$ (6 mmol), CO (50 atm), $Ru_3(CO)_{12}$ (0.02 mmol), PCy_3 (0.06 mmol), CH_3CN (10 mL), 140 °C, 20 h. The group E stands for COOEt. [b] Isolated yield based on the diyne.

The strongest support for Scheme I comes from a stoichiometric reaction reported by Katz of methylcarbyne complexes $(CO)_4BrM{\equiv}CCH_3$ (M = Cr and W) with diyne **1a** to give a similar product.[11] All of these precedents suggest the intervention of a siloxy(or hydroxy[12]) carbyne complex **5** in the present catalytic reaction (eq 4). Nicholas proposed, without experimental support, that a 1,3-hydrogen shift from a metal to the oxygen atom of the CO ligand in metal carbonyls might be an important step in homogeneous transition-metal-catalyzed CO reduction.[13] We believe that the catalytic cycle outlined in Scheme I is reasonable, and it represents the first example of the oxycarbyne-based catalytic cycle.[14]

The catalytic reaction provides a useful synthetic method for fused-ring catechol derivatives. For synthetic purposes, the reaction conditions of run 4 in Table I are adopted since they gave only one relatively air and moisture stable product in higher yields. The representative results are shown in Table II, and these indicate the potential utility of the present catalytic reaction.[15] Functional groups such as ester, ketone, ether, and amide were compatible in the present reaction. The yields were not affected by the presence of an alkyl group attached to the terminal acetylenic carbon (entries 6 and 7). A disubstituted diyne **1h** reacted similarly but gave a monosilylated catechol **2h** as a byproduct even when a prolonged reaction time was used (entry 7). The formation of a fused six-membered ring was not observed from a 1,7-diyne system.

The present reaction represents the first catalytic reaction involving the intermediary of an oxycarbyne complex as the key catalytic species and also the first example of successive incorporation of two molecules of CO into diynes. A third way of activation/bond formation of CO, shown here, will open up new fields for carbonylation. Experiments designed to detect, trap, and isolate siloxy(or hydroxy)carbyne complexes are underway.

Supplementary Material Available: Listings of spectral data and elemental analyses for the products (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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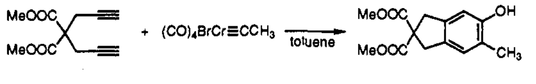

(12) Whether SiR_3 or H migrates is not clear at the present time. A topologically similar intramoleculer 1,3-hydrogen shift has been observed in alkynylcobalt complexes. Bianchini, C.; Peruzzini, M.; Vacca, A.; Zanobini, F. *Organometallics* **1991**, *10*, 3697.

(13) Nicholas, K. M. *Organometallics* **1982**, *1*, 1713.

(14) Carbyne complexes have been postulated as a catalytic key species in metathesis of acetylenes. See refs 8b,c.

(15) A large number of natural products, in particular antitumor agents, possess catechol or o-quinone as a subunit. Tisler, M. *Adv. Heterocycl. Chem.* **1989**, *45*, 37.