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Alkynes as Allylmetal Equivalents in Redox-Triggered C−C Couplings to Primary Alcohols: (*Z*)-Homoallylic Alcohols via Ruthenium-Catalyzed Propargyl C−H Oxidative Addition

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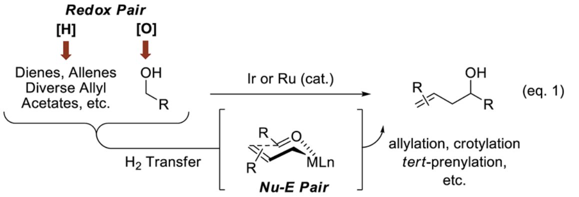
Supporting Information

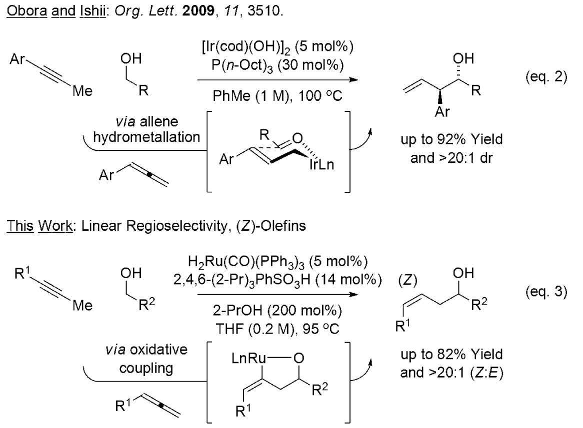
ABSTRACT: The cationic ruthenium catalyst generated upon the acid−base reaction of $H_2Ru(CO)(PPh_3)_3$ and 2,4,6-(2-Pr)$_3$PhSO$_3$H promotes the redox-triggered C−C coupling of 2-alkynes and primary alcohols to form (*Z*)-homoallylic alcohols with good to complete control of olefin geometry. Deuterium labeling studies, which reveal roughly equal isotopic compositions at the allylic and distal vinylic positions, along with other data, corroborate a catalytic mechanism involving ruthenium(0)-mediated allene−aldehyde oxidative coupling to form a transient oxaruthenacycle, an event that ultimately defines (*Z*)-olefin stereochemistry.

Allylative carbonyl additions represent a major class of C−C bond formations that have found broad use in chemical synthesis.[1] The majority of methods rely upon use of preformed allylmetal reagents or, as exemplified in Nozaki−Hiyama−Kishi-type allylations, stoichiometric quantities of (organo)-metallic reductant.[2] By harnessing the native reducing capability of alcohols, we have developed a broad, new class of redox-triggered carbonyl allylations that bypass use of stoichiometric (organo)metallic reagents (eq 1).[3] In the course of our studies,



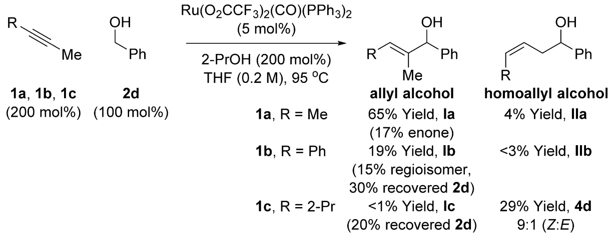
Obora and Ishii reported a remarkable iridium-catalyzed C−C coupling of 1-aryl-1-propynes to furnish branched products of carbonyl allylation (Scheme 1, eq 2).[4] Such branched products of allylation are formed in related iridium-[5a] and ruthenium-catalyzed[5b] C−C couplings of primary alcohols and allenes, suggesting alkyne-to-allene isomerization is evident in this process. These observations, in combination with our ongoing studies of the ruthenium-catalyzed C−C coupling of alkynes and primary alcohols or aldehydes to form allylic alcohols or enones,[6] prompted us to explore the use of alkynes as allyl donors[7] under the conditions of ruthenium catalysis. Here, we report that the cationic ruthenium complexes generated through the acid−base reaction of $H_2Ru(CO)(PPh_3)_3$ and 2,4,6-(2-Pr)$_3$PhSO$_3$H catalyzes[8] the redox-triggered C−C coupling of alkynes and primary alcohols to furnish (*Z*)-homoallylic alcohols with good to complete control of olefin geometry (Scheme 1, eq 3). Mechanistic studies implicate intervention of a novel alkylidene ruthenacyclopropane intermediate.

Scheme 1. 2-Alkynes as Allylmetal Equivalents in Redox-Triggered C−C Couplings of Primary Alcohols



In initial experiments (Scheme 2), 2-butyne **1a** and benzyl alcohol **2d** were exposed to our previously reported conditions for ruthenium-catalyzed alcohol−alkyne C−C coupling to form allylic alcohol **Ia** to determine whether trace quantities of allylation product were evident.[6a] The previously observed products of vinylation, allylic alcohol **Ia** and enone *dehydro*-**Ia**, were generated in 65% and 17% yield, respectively. Along with these materials, careful analysis of the ^{1}H NMR spectra of **Ia** did indeed reveal trace quantities of (*Z*)-homoallylic alcohol **IIa**.

Scheme 2. Observation of (*Z*)-Allylation Pathways in Ruthenium-Catalyzed C−C Couplings of Alkynes and Primary Alcohols



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Variation of the alkyne was explored as a potential means of partitioning the vinylation and (*Z*)-allylation pathways. Upon use of 4-methyl-2-pentyne **1c**, the vinylation pathway was suppressed and the product of (*Z*)-allylation **4d** was formed in 29% isolated yield as a 9:1 (*Z*:*E*) mixture of geometrical isomers. Encouraged by this result, optimization of the (*Z*)-allylation pathway was undertaken. Eventually, it was found that the ruthenium(II) catalyst prepared *in situ* from the acid–base reaction of $H_2Ru(CO)(PPh_3)_3$ and 2,4,6-tri(2-propyl)-phenylsulfonic acid hydrate[8,9] $(ArSO_3)_2Ru(CO)(PPh_3)_2$ delivered the best results, providing the (*Z*)-homoallylic alcohol **4c** in 70% yield as a single geometrical isomer, as determined by ^1H NMR. Due to competing conventional alcohol–alkyne transfer hydrogenation, 2-propanol (200 mol%) is required to promote higher conversion. For the reaction of 4-methyl-2-pentyne **1c** and 4-bromobenzyl alcohol **2c** conducted in the absence of 2-propanol, the (*Z*)-homoallylic alcohol **4c** is obtained in roughly 40% isolated yield along with substantial quantities of unreacted aldehyde **3c**. 2-Propanol is postulated to convert unreacted aldehyde back to the kinetically more reactive primary alcohol, resetting the "redox trigger".

Under these conditions, the reaction of 4-methyl-2-pentyne **1c** with electron-deficient and electron-neutral benzylic alcohols **2a-2d** and **2g-2i** occurs smoothly to furnish the (*Z*)-homoallylic alcohol **4a–4d** and **4g–4i** in moderate to good yield with complete levels of olefin stereocontrol, as determined by ^1H NMR (Table 1). As illustrated in the coupling of benzylic alcohols **2e** and **2f**, which incorporate 4-methyl and 4-methoxy substituents, the efficiency of this process decreases with increasing electron richness of the transient aldehyde, yet 2-methoxy benzyl alcohol **2i** provides a moderate yield of adduct **4i**. Aliphatic alcohols **2j–2o** provide moderate to good yields of the (*Z*)-homoallylic alcohols **4j–4o**. The coupling is effective for alcohols with adjacent secondary, tertiary, and even quaternary carbon centers, albeit with incomplete levels of (*Z*)-olefin stereocontrol. To further probe the scope of this process, cyclohexyl-, *tert*-butyl-, and 2-phenyl-2-propyl-substituted alkynes **1d–1f** were surveyed. Exposure of alkynes **1d–1f** to alcohols **2c** and **2j** under standard reaction conditions delivered the products of (*Z*)-allylation **4p–4r** and **4s–4u**, respectively, in good yields with good levels of (*Z*)-olefin stereocontrol (Table 2). Finally, as illustrated in the reaction of 4-methyl-2-pentyne **1c** and *p*-bromobenzaldehyde **3c**, identical products of (*Z*)-allylation are accessible from the aldehyde oxidation level under standard reaction conditions (eq 4).

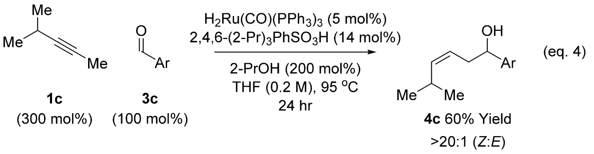
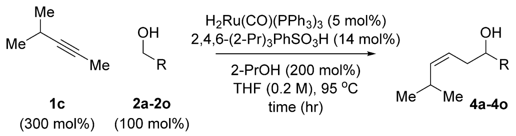
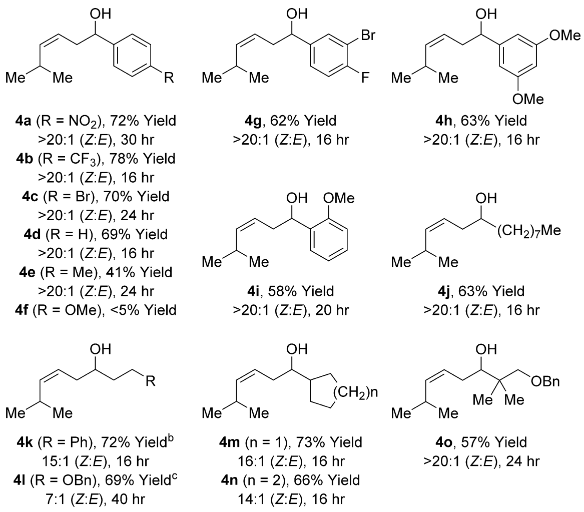


Table 1. Redox-Triggered C–C Coupling of Alkyne 1c and Alcohols 2a–2o To Form (Z)-Homoallylic Alcohols 4a–4o[a]



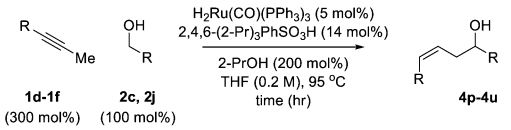
2a, R = 4-NO_2Ph	**2b**, R = 4-CF_3Ph	**2c**, R = 4-BrPh	**2d**, R = Ph
2e, R = 4-MePh	**2f**, R = 4-MeOPh	**2g**, R = 3-Br,4-FPh	**2h**, R = 3,5-(MeO)$_2$Ph
2i, R = 2-MeOPh	**2j**, R = $(CH_2)_7Me$	**2k**, R = $(CH_2)_2Ph$	**2l**, R = $(CH_2)_2OBn$
2m, R = cyclopentyl	**2n**, R = cyclohexyl	**2o**, R = $C(CH_3)_2CH_2OBn$	

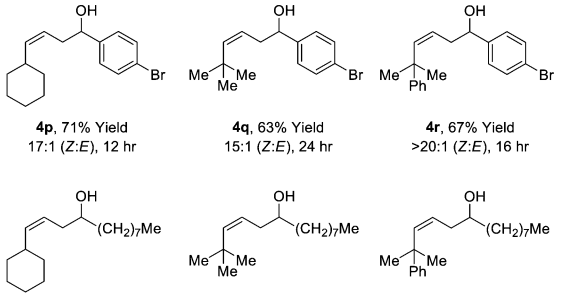


4a (R = NO_2), 72% Yield >20:1 (*Z*:*E*), 30 hr
4b (R = CF_3), 78% Yield >20:1 (*Z*:*E*), 16 hr
4c (R = Br), 70% Yield >20:1 (*Z*:*E*), 24 hr
4d (R = H), 69% Yield >20:1 (*Z*:*E*), 16 hr
4e (R = Me), 41% Yield >20:1 (*Z*:*E*), 24 hr
4f (R = OMe), <5% Yield
4g, 62% Yield >20:1 (*Z*:*E*), 16 hr
4h, 63% Yield >20:1 (*Z*:*E*), 16 hr
4i, 58% Yield >20:1 (*Z*:*E*), 20 hr
4j, 63% Yield >20:1 (*Z*:*E*), 16 hr
4k (R = Ph), 72% Yield[b] 15:1 (*Z*:*E*), 16 hr
4l (R = OBn), 69% Yield[c] 7:1 (*Z*:*E*), 40 hr
4m (n = 1), 73% Yield 16:1 (*Z*:*E*), 16 hr
4n (n = 2), 66% Yield 14:1 (*Z*:*E*), 16 hr
4o, 57% Yield >20:1 (*Z*:*E*), 24 hr

[a] Yields are of material isolated by silica gel chromatography. See Supporting Information for further experimental details. [b] $H_2Ru(CO)(PPh_3)_3$ (7.5 mol%), 2,4,6-(2-Pr)$_3$PhSO$_3$H (21 mol%). [c] $Ru(O_2CCF_3)_2(CO)(PPh_3)_2$ (10 mol%), omit 2,4,6-(2-Pr)$_3$PhSO$_3$H.

Table 2. Redox-Triggered C–C Coupling of Alkynes 1d–1f and Alcohols 2c and 2j To Form (Z)-Homoallylic Alcohols 4p–4u[a]





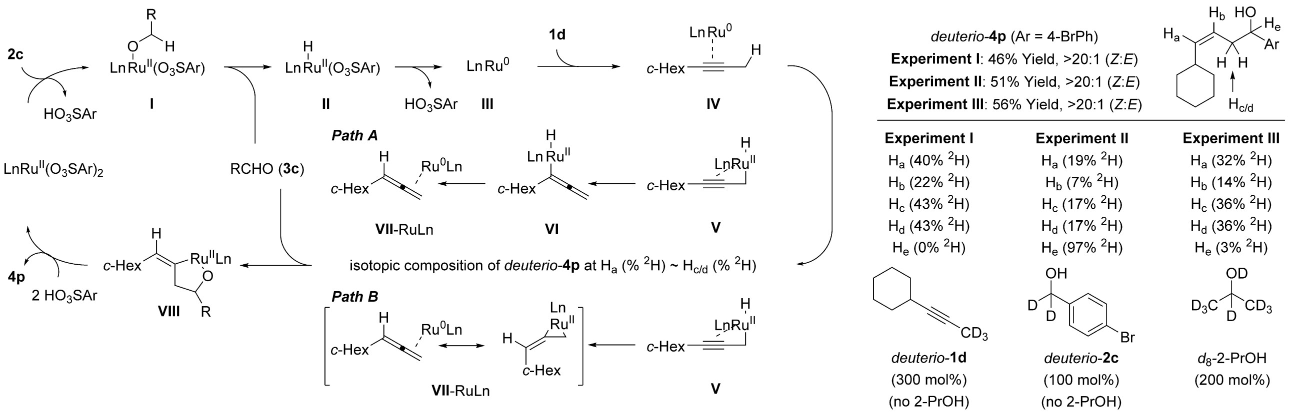
1d, R = *c*-Hex	**1e**, R = *t*-Bu	**1f**, R = CMe_2Ph
4p, 71% Yield 17:1 (*Z*:*E*), 12 hr	**4q**, 63% Yield 15:1 (*Z*:*E*), 24 hr	**4r**, 67% Yield >20:1 (*Z*:*E*), 16 hr
4s, 82% Yield 10:1 (*Z*:*E*), 16 hr	**4t**, 77% Yield 8:1 (*Z*:*E*), 16 hr	**4u**, 80% Yield 11:1 (*Z*:*E*), 16 hr

[a] Yields are of material isolated by silica gel chromatography. See Supporting Information for further experimental details.

Using the present catalyst system, less hindered 2-alkynes such as 2-pentyne react with alcohols through conventional transfer hydrogenation pathways to form aldehyde products. Use of 3-alkynes such as 1-cyclopentyl-1-butyne provides a 21% isolated yield of C–C coupling product with excellent (*Z*)-stereoselectivity but as a mixture of regio- and diastereomers.

To gain insight into the catalytic mechanism and the origins of (*Z*)-olefin stereoselectivity, a series of deuterium labeling studies were performed. In one experiment, the deuterium-labeled alkyne, *deteurio*-**1d**, was employed as a reactant in the absence of 2-propanol under otherwise standard conditions. In a second experiment, the deuterium-labeled alcohol, *deuterio*-**2c**, was employed as a reactant in the absence of 2-propanol. Finally, the unlabeled alkyne **1d** and alcohol **2c** were reacted

Scheme 3. Deuterium Labeling Studies and Proposed General Catalytic Mechanism Accounting for (*Z*)-Stereoselectivity and the Roughly Equal Isotopic Compositions at H_a, H_c, and H_d in Different Labeling Experiments[a]

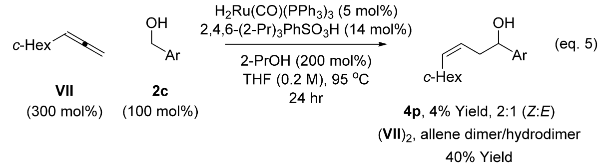


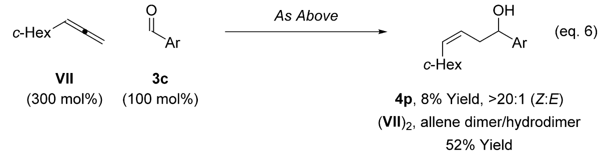
[a] The extent of ^2H incorporation was determined using ^1H and ^2H NMR. For the deuterium labeling experiments, reactions were conducted under standard conditions except for the indicated changes. See Supporting Information for further experimental details, including equations accounting for the regioselectivity and extent of deuterium incorporation at positions H_a–H_e.

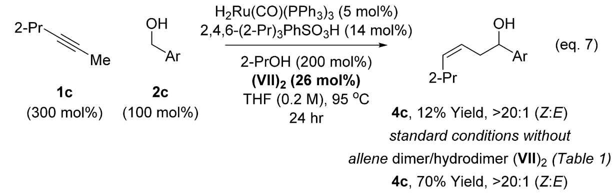
with d_8-2-propanol. For each experiment, the pattern of deuterium incorporation evident in the reaction product, *deuterio*-**4p**, was determined by ^1H and ^2H NMR spectroscopy (Scheme 3). *Notably, the isotopic composition at the vinylic hydrogen H_a is roughly equivalent to the isotopic composition of the allylic hydrogens H_c and H_d for each experiment.*

On the basis of these data, the indicated catalytic mechanism was proposed (Scheme 3). The ruthenium bis-sulfonate complex $LnRu^{II}(O_3SAr)_2$ reacts with alcohol **2c** to form the ruthenium alkoxide **I**. *β*-Hydride elimination from alkoxide **I** provides the aldehyde **3c** and the hydridoruthenium sulfonate **II**, which upon loss of HO_3SAr delivers the zerovalent ruthenium complex **III**. Such alcohol mediated reductions of $LnRu^{II}(X)_2$ to $LnRu^0$ have been described.[10] Propargyl C–H oxidative addition from alkyne complex **IV** delivers the propargyl complex **V**, which undergoes reductive elimination from the allenylruthenium hydride **VI** (Path A)[11] to provide the allene **VII**.[12,13] Allene–carbonyl oxidative coupling provides the oxaruthenacycle **VIII**,[14] defining the olefin (*Z*)-stereochemistry. Protonolytic cleavage of the metallacycle delivers the (*Z*)-homoallylic alcohol **4p** and regenerates $LnRu^{II}(O_3SAr)_2$ to close the catalytic cycle. Alternatively, the propargyl hydride complex **V** may hydrometallate internally (Path B) to form the indicated alkylidine ruthenacyclopropane, which is a mesomeric form of **VII**-RuLn by virtue of *π*-backbonding.[15] Mechanisms involving intervention of homopropargylic alcohols were considered, but appear inconsistent with the observed patterns of deuterium incorporation.

To challenge the veracity of this interpretation of the mechanism, allene **VII** was subjected to standard coupling conditions with alcohol **2c** (eq 5) and aldehyde **3c** (eq 6). In each experiment, the product of (*Z*)-allylation **4p** was formed in small quantities along with a substantial amount of allene dimerization[16] (possibly [2+2] cycloadducts)[16b] and hydrodimerization[17] products $(\mathbf{VII})_2$,[18,19] which appear as a complex mixture of isomers as determined by HRMS and GC-MS analysis (see Supporting Information). Unreacted allene **VII** was not detected. Finally, whereas reaction of alkyne **1c** with alcohol **2c** under standard conditions provides the (*Z*)-homoallylic alcohol **4c** in 70% yield (Table 1), the same reaction conducted in the presence of allene dimer/hydrodimer $(\mathbf{VII})_2$ provides a 12% yield of **4c** (eq 7). Thus, competing allene dimerization and hydrodimerization not only diverts material to alternate reaction products, but the allene dimer/hydrodimer $(\mathbf{VII})_2$ itself suppresses the (*Z*)-allylation pathway, making reactions involving stoichiometric loadings of allene **VII** intrinsically less efficient. These data suggest one important feature of the present catalytic system is that the requisite allene does not accumulate, but is generated transiently in a pairwise fashion with the aldehyde. A low steady state concentration of allene is important to suppress ruthenium-catalyzed allene dimerization,[16,18] hydrodimerization[17] or thermally promoted allene [2+2] cycloaddition,[19] to produce dimers that poison the catalyst.







In summary, exposure of 2-alkynes and alcohols to the ruthenium catalyst generated *in situ* upon the acid–base reaction of $H_2Ru(CO)(PPh_3)_3$ and 2,4,6-(2-Pr)$_3$PhSO$_3$H results in the formation of (*Z*)-homoallylic alcohols with good to complete control of olefin geometry. In a series of deuterium labeling experiments, roughly equal isotopic composition is observed at the allylic and distal vinylic positions of the product, corroborating a catalytic mechanism wherein alkyne-to-allene isomerization precedes allene–carbonyl oxidative coupling to form a geometrically defined oxaruthenacycle. These studies contribute to the growing body of redox-triggered alcohol C–C couplings—new carbonyl addition chemistry that extends beyond the use of premetalated reagents.[3]

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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