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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Enantioselective Ruthenium-Catalyzed Carbonyl Allylation via Alkyne–Alcohol C–C Bond-Forming Transfer Hydrogenation: Allene Hydrometalation vs Oxidative Coupling

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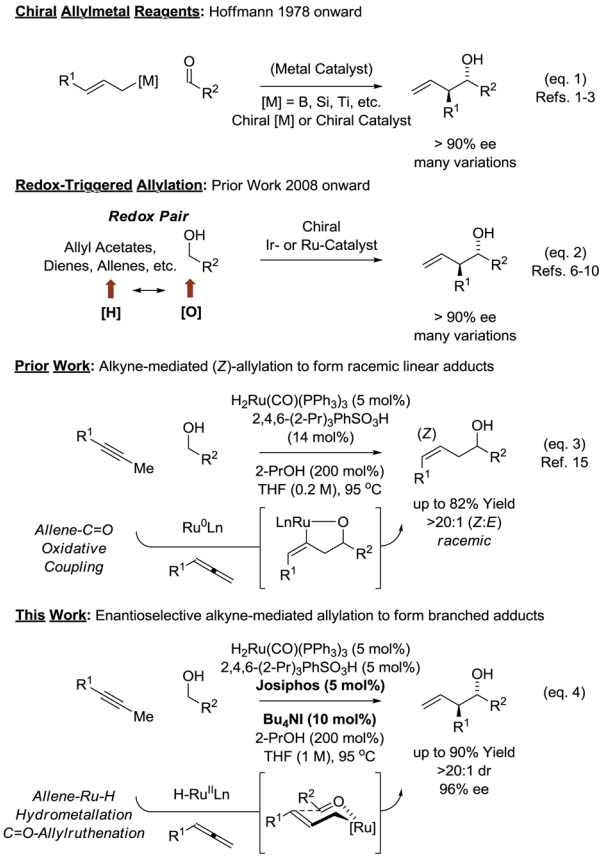
Supporting Information

ABSTRACT: Chiral ruthenium(II) complexes modified by Josiphos ligands catalyze the reaction of alkynes with primary alcohols to form homoallylic alcohols with excellent control of regio-, diastereo-, and enantioselectivity. These processes represent the first examples of enantioselective carbonyl allylation using alkynes as allylmetal equivalents.

Enantioselective carbonyl allylation is of broad use in chemical synthesis.[1] As exemplified in the seminal work of Hoffmann in 1978,[2a] preformed allylmetal reagents modified by chiral auxiliaries are effective in enantioselective carbonyl allylation (Scheme 1, eq 1).[2] Alternatively, as first demonstrated by Yamamoto (1991), achiral allylmetal reagents can used in combination with chiral catalysts (Scheme 1, eq 1).[3] Finally, enantioselective carbonyl allylation can be achieved through the reductive coupling of allylic halides, as in Nozaki–Hiyama–Kishi type allylations,[4] and umpoled reactions of allylic carboxylates under the conditions of metal catalysis.[5] The latter reaction type typically requires stoichiometric metallic or metal-based reductants. Exploiting hydrogen embedded in alcohol reactants, we have developed redox-neutral enantioselective carbonyl allylations,[6] wherein alcohol oxidation is coupled to reductive cleavage of allylic carboxylates[7] or the hydrometalation of dienes,[8] allenes,[9] or enynes[10] to generate aldehyde–organometal pairs (Scheme 1, eq 2).

In the course of our studies, Obora and Ishii reported the iridium-catalyzed reaction of 1-aryl-1-propynes with alcohols to form racemic products of carbonyl allylation.[11] Having encountered such products in allene-alcohol C–C couplings catalyzed by iridium[9] and ruthenium,[12] alkyne-to-allene isomerization is likely operative in this process. The possibility of promoting such transformations using a *ruthenium* catalyst appeared tenuous, as established alkyne-alcohol C–C couplings are known to form allylic alcohols.[13,14] Despite this precedent, we recently found that ruthenium catalysts generated upon the acid–base reaction of $H_2Ru(CO)(PPh_3)_3$ and 2,4,6-$(2\text{-}Pr)_3PhSO_3H$ convert 2-alkynes and primary alcohols to (*Z*)-homoallylic alcohols through pathways involving alkyne-to-allene isomerization with subsequent allene–carbonyl oxidative coupling (Scheme 1, eq 3).[15] In this Communication, we disclose key alterations to the reaction conditions that suppress allene-carbonyl oxidative coupling of the transient allene to favor allene hydrometalation,[16] resulting in the first examples of catalytic enantioselective carbonyl allylation using alkynes as chiral allylmetal equivalents (Scheme 1, eq 4).[17]

Scheme 1. Strategies for Enantioselective Carbonyl Allylation

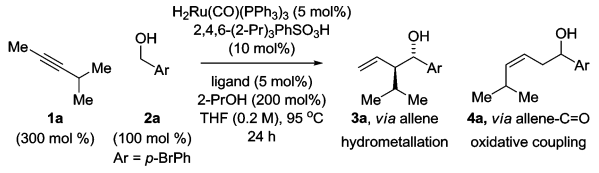


Under established conditions for the ruthenium-catalyzed coupling of 4-methyl-2-pentyne **1a** with *p*-bromobenzyl alcohol **2a**, the linear (*Z*)-homoallylic alcohol **4a** is generated in 70% isolated yield as a single alkene stereoisomer (Table 1, entry 1). It was found that introduction of Bu_4NI (10 mol%) inhibited conversion to the (*Z*)-homoallylic alcohol **4a** (Table 1, entry 2). Using the chelating phosphine ligand dppf in the absence of Bu_4NI, roughly equimolar quantities of the branched allylation product **3a** and the (*Z*)-homoallylic alcohol **4a** were obtained

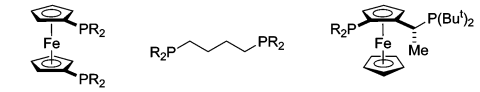
Received: January 22, 2015
Published: March 3, 2015

DOI: 10.1021/jacs.5b00747
J. Am. Chem. Soc. 2015, 137, 3161–3164

Table 1. Selected Experiments Illustrating the Partitioning of Hydrometalative and Oxidative Coupling Pathways in the Reaction of 1a and 2a to Form Isomers 3a and 4a[a]



Entry	Bu_4NI	ligand	3a (yield, dr)	4a (yield, Z:E)
1[b]	-	-	-	70%, >20:1
2	(10 mol%)	-	-	24%, 10:1
3	-	dppf	21%, 7:1	16%, 5:1
4	(10 mol%)	dppf	83%, 15:1	-
5	(10 mol%)	dippf	57%, >20:1	-
6	(10 mol%)	dppb	36%, 13:1	-
7	(10 mol%)	dCypb	49%, >20:1	-
8	(10 mol%)	SL-J009-1	59%, >20:1, 84% ee	-
9	(10 mol%)	SL-J002-1	86%, >20:1, 80% ee	-
10[c]	(10 mol%)	SL-J002-1	86%, >20:1, 94% ee	-
11[c,d]	(10 mol%)	SL-J009-1	79%, >20:1, 94% ee	-

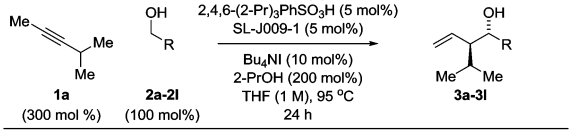


[a]Yields are of material isolated by silica gel chromatography. See Supporting Information for further experimental details. [b]2,4,6-(2-Pr)$_3$PhSO$_3$H (14 mol%). [c]2,4,6-(2-Pr)$_3$PhSO$_3$H (5 mol%). [d]THF (1 M).

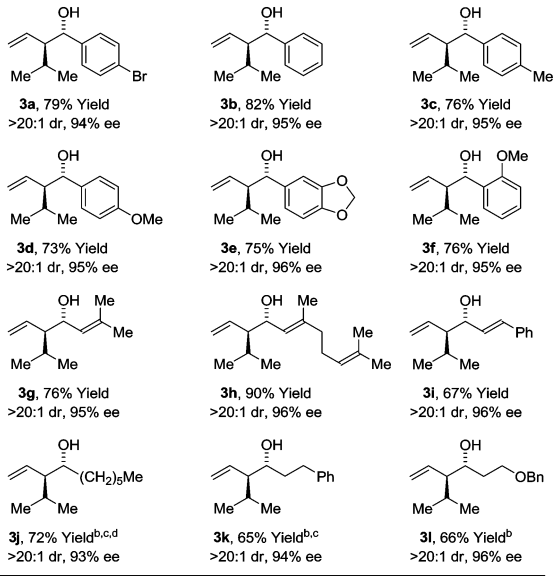
in modest yield (Table 1, entry 3). To our delight, the combination of Bu_4NI and dppf led to an 83% yield of the branched allylation product **3a** as a 15:1 (*anti*:*syn*) diastereomeric mixture (Table 1, entry 4). Using dippf as ligand, the branched allylation product **3a** was formed as a single *anti*-diastereomer in 57% yield (Table 1, entry 5). In general, *P*-alkyl-substituted chelating ligands provided superior levels of diastereoselectivity compared to their *P*-phenyl congeners (Table 1, entry 4 vs 5; entry 6 vs 7). At this stage, diverse chiral chelating phosphine ligands were evaluated. Promising levels of asymmetric induction were observed using the Josiphos ligands SL-J009-1 and SL-J002-1 (Table 1, entries 8 and 9). Lowering the loading of 2,4,6-tri(2-propyl)-phenylsulfonic acid (5 mol%),[18,19] the branched allylation product **3a** could be obtained in excellent yield and 94% enantiomeric excess (ee) using either SL-J009-1 or SL-J002-1 as ligand (Table 1, entries 10 and 11). Omission of 2,4,6-tri(2-propyl)phenylsulfonic acid led to over-oxidation of **3a** to form ketones, that is, products of allene hydroacylation.[14] Omission of 2-PrOH led to a roughly 20% reduction in yield of **3a** and accumulation of unreacted aldehyde, dehydro-**2a**.

With these optimized conditions in hand, diverse alcohols **2a**–**2l** were surveyed for their ability to participate in this new protocol for asymmetric allylation (Table 2). Benzylic alcohols **2a**–**2f** were converted to adducts **3a**–**3f**, respectively, in good yield with complete levels of *anti*-diastereoselectivity and uniformly high levels of enantiomeric enrichment (94–96% ee). Allylic alcohols **2g**–**2i** could potentially engage in internal redox isomerization to form the corresponding aldehydes,[20] but such products are not observed. Rather, adducts **3g**–**3i** are formed in a highly regio- and stereoselective manner. Similarly high levels of selectivity were observed in the conversion of aliphatic alcohols **2j**–**2l** to adducts **3j**–**3l**. Under these first-generation conditions, branched primary alcohols such as

Table 2. Regio-, *anti*-Diastereo-, and Enantioselective C–C Coupling of Alkyne 1a and Alcohols 2a–2l to Form Branched Products of Carbonyl Allylation 3a–3l[a]



2a, R = 4-BrPh; **2b**, R = Ph; **2c**, R = 4-MePh; **2d**, R = 4-MeOPh
2e, R = 4-piperonyl; **2f**, R = 2-MeOPh; **2g**, R = HC=CMe$_2$; **2h**, geraniol
2i, R = HC=CH(Ph); **2j**, R = (CH$_2$)$_5$Me; **2k**, R = (CH$_2$)$_2$Ph; **2l**, R = (CH$_2$)$_2$OBn



[a]Yields are of material isolated by silica gel chromatography. Diastereoselectivities were determined by ^{1}H NMR analysis of crude reaction mixtures. See Supporting Information for further experimental details. [b]2-PrOH was omitted. [c]125 °C. [d]48 h.

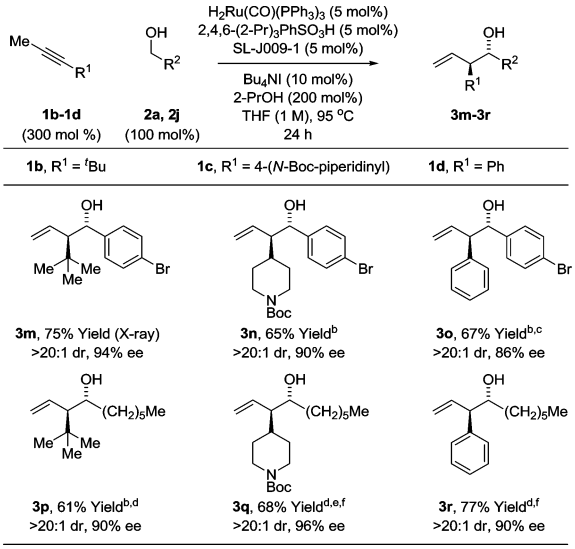
isobutyl alcohol provided adducts in the range of 30–40% yield. Under these conditions, secondary alcohols oxidize to form ketone products and do not engage in C–C coupling.

To further explore the scope of this method for catalytic enantioselective allylation, a series of substituted propynes **1b**-**1d** possessing *tert*-butyl (**1b**), 4-(*N*-Boc-piperidinyl) (**1c**), and phenyl (**1d**) moieties were explored in couplings to benzylic alcohol **2a** and aliphatic alcohol **2j** (Table 3). In the case of the *tert*-butyl-substituted alkyne **1b**, adducts **3m** and **3p** were generated in good yield with complete levels of *anti*-diastereoselectivity and excellent levels of enantioselectivity, 94% ee and 90% ee, respectively. Similarly, for 4-(*N*-Boc-piperidinyl)-substituted alkyne **1c**, adducts **3n** and **3q** were formed with good control of relative and absolute stereochemistry, despite potential cleavage of the acid-sensitive Boc-protecting group. Finally, the phenyl-substituted alkyne **1d** coupled to alcohols **2a** and **2j** to provide adducts **3o** and **3r**, respectively, in good yield as single diastereomers and good to excellent control of enantioselectivity, 86% ee and 90% ee, respectively. Attempted use of 2-pentyne resulted in a complex mixture of products. The relative and absolute stereochemical assignment of adducts **3a**-**3r** is made in analogy adduct **3m**, which was determined by single-crystal X-ray diffraction analysis.

A general catalytic mechanism was proposed (Scheme 2). Allene hydrometalation forms a nucleophilic allylruthenium complex. The stoichiometric reaction of HXRu(CO)(PR$_3$)$_3$ (X

DOI: 10.1021/jacs.5b00747
J. Am. Chem. Soc. 2015, 137, 3161–3164

Table 3. Regio-, *anti*-Diastereo-, and Enantioselective C−C Coupling of Alkynes 1b−1d and Alcohols 2a and 2j to Form Branched Products of Carbonyl Allylation 3m−3r[a]



[a]Yields are of material isolated by silica gel chromatography. Diastereoselectivities were determined by ^{1}H NMR analysis of crude reaction mixtures. See Supporting Information for further experimental details. [b]72 h. [c]75 °C. [d]2-PrOH was omitted. [e]7.5 mol% of $H_2Ru(CO)(PPh_3)_3$, $ArSO_3H$, SL-J009-1, and 15 mol% Bu_4NI. [f]48 h.

= Cl, Br) with allenes to form π-allylruthenium complexes is known.[21] We have found that such π-allylruthenium species are highly fluxional in nature, undergoing rapid geometrical isomerization by way of the σ-bound haptomers.[12] Coordination of aldehyde to the pentacoordinate (E)-σ-allylruthenium species leads to stereospecific addition through a closed transition structure to form the homoallylic ruthenium alkoxide. Protonolytic cleavage of the alkoxide by the arylsulfonic acid releases the product and provides the indicated ruthenium sulfonate, which is displaced by a primary alcohol. Subsequent β-hydride elimination generates aldehyde along with the ruthenium hydride to close the catalytic cycle. Notably, in the absence of acid, β-hydride elimination occurs at the stage of the homoallylic ruthenium alkoxide to furnish the β,γ-enone.[14] Hence, substoichiometric arylsulfonic acid appears to catalyze alkoxide exchange at the metal center. Using $HIRu(CO)(PR_3)_3$ as precatalyst in the absence of arylsulfonic acid under otherwise standard conditions, alcohol **2a** is converted to the branched allylation product **3a** in 68% yield, >20:1 dr, and 81% ee, corroborating intervention of iodide as a counterion for ruthenium. The strong σ-donicity of iodide may destabilize ruthenium(0), suppressing competitive oxidative coupling pathways. The indicated deuterium labeling experiments are consistent with this interpretation of the mechanism, and further reveal that the reaction products are inert with respect to alcohol dehydrogenation, which prevents any erosion in kinetic stereoselectivity under the reaction conditions. It should be noted that protons from the reactant alcohol or adventitious water may contribute to diminished levels of deuterium incorporation.[22]

In summary, we report a ruthenium-catalyzed enantioselective carbonyl allylation wherein alkynes and primary alcohols serve as redox pairs. A notable feature of these transformations is the use of alkynes as a reservoir for allenes, which are kinetically more reactive and which form *in situ* through a second, parallel ruthenium-catalyzed isomerization process. Of further note are the subtle changes in reaction conditions that enable partitioning of two competing catalytic pathways, allene−carbonyl oxidative coupling vs allene hydrometalation, while the parallel ruthenium-catalyzed alkyne isomerization pathway is maintained. More broadly, this work contributes to a growing body of catalytic processes developed in our laboratory wherein the native reducing ability of alcohols is used to generate transient organometallics from π-unsaturated precursors, enabling carbonyl addition from the alcohol oxidation level in the absence of stoichiometric organometallic reagents.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and spectral data; HPLC traces corresponding to racemic and enantiomerically enriched samples; single-crystal X-ray diffraction data for compound **3m**. This material is available free of charge via the Internet at http://pubs.acs.org.

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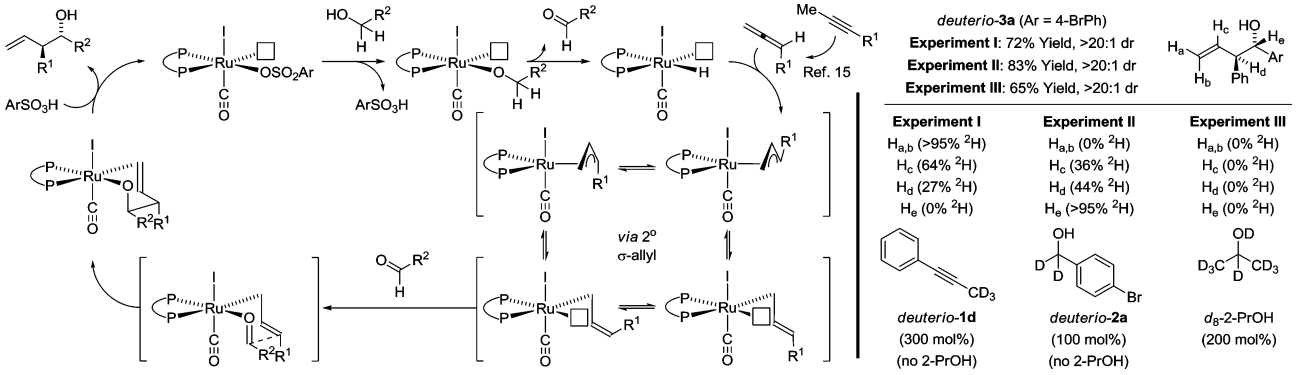
Scheme 2. Deuterium Labeling Studies and General Catalytic Mechanism[a]



[a]The extent of ^{2}H incorporation was determined using ^{1}H and ^{2}H NMR. For the deuterium labeling experiments, reactions were conducted using dippf as ligand. See Supporting Information for further experimental details, including equations accounting for the regioselectivity and extent of deuterium incorporation at positions H_a−H_e.

DOI: 10.1021/jacs.5b00747
J. Am. Chem. Soc. 2015, 137, 3161−3164

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The Robert A. Welch Foundation (F-0038) and the NIH-NIGMS (RO1-GM069445) are acknowledged for partial support of this research.

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DOI: 10.1021/jacs.5b00747
J. Am. Chem. Soc. 2015, 137, 3161–3164