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A Metallacycle Fragmentation Strategy for Vinyl Transfer from Enol Carboxylates to Secondary Alcohol C-H Bonds *via* Osmium or Ruthenium Catalyzed Transfer Hydrogenation

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Abstract

A strategy for catalytic vinyl transfer from enol carboxylates to activated secondary alcohol C-H bonds is described. Using XPhos-modified ruthenium(0) or osmium(0) complexes, enol carboxylate-carbonyl oxidative coupling forms transient β -carboxy-oxametallacycles, which eliminate carboxylate to deliver allylic ruthenium(II) or osmium(II) alkoxides. Reduction of the metal(II) salt *via* hydrogen transfer from the secondary alcohol reactant releases the product of carbinol C-H vinylation and regenerates ketone and zero-valent catalyst.

Graphical abstract

Carbonyl vinylation is a convergent method for the synthesis of allylic alcohols that often relies on the stoichiometric use of vinylmetal reagents (Scheme 1, eq. 1).¹ Metal catalyzed alkyne-carbonyl reductive coupling^{2,3} bypasses discrete use of vinylmetal reagents, however, with the exception of hydrogen-mediated processes,³ stoichiometric reductants that are metallic, pyrophoric and mass-intensive are often required (Scheme 1, eq. 2).² More recently, redox-neutral alcohol-alkyne vinylation have been developed using ruthenium^{4a,b} and nickel catalysts (Scheme 1, eq. 3).^{4c} Despite these important advances, efficient catalysts for the reductive coupling of acetylene and terminal alkynes to carbonyl partners remain elusive.⁵ The E1cB-type fragmentation of metallacycles bearing leaving groups vicinal to the metal potentially offers an alternate strategy for vinyl transfer, which, to date, has only been realized in *stoichiometric* reactions of early transition metals.^{6,7} Here, we introduce a general strategy for *catalytic* vinyl transfer from enol carboxylates to activated

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Supporting Information Available: Experimental procedures and spectral data. This material is available free of charge *via* the internet at <http://pubs.acs.org>.

ketones based on oxidative coupling-metallacycle fragmentation pathways (Scheme 1, eq. 4).⁸ This method enables direct vinylation of secondary alcohol C-H bonds in vicinally dioxygenated systems (e.g. α -hydroxy esters, 1,2-diols), including the introduction of unsubstituted vinyl moieties.

Initial experiments involving the reaction of ethyl mandelate **1a** with vinyl acetate **2a** were inspired by established conditions for ruthenium(0) catalyzed C-C couplings of activated secondary alcohols with 1,3-dienes,⁹ and earlier studies by Chatani and Murai on the ruthenium(0) catalyzed Pauson-Khand reaction of vicinal dicarbonyl compounds.¹⁰ Control experiments in the absence of the precatalyst components revealed small quantities of acyl transfer to form *O*-Ac-**1a** (Table 1, entries 1 and 2). In the presence of Ru₃(CO)₁₂ and XPhos, ethyl mandelate **1a** and vinyl acetate **2a** reacted to form a 1:1 mixture of the desired product of vinyl transfer **3a** and *O*-Ac-**1a** in a combined 29% isolated yield (Table 1, entry 3). Remarkably, the use of Os₃(CO)₁₂ and XPhos under otherwise identical conditions provided an 85% isolated yield of vinyl transfer product **3a** and *O*-Ac-**1a** in a 9.5:1 (Table 1, entry 4). The enhanced performance of osmium(0) catalyst¹¹ can be understood on the basis of π -backbonding.¹² In an effort to suppress competing formation of *O*-Ac-**1a**, the use of vinyl pivalate **2a** was explored (Table 1, entries 5 and 6). The reaction of ethyl mandelate **1a** with vinyl pivalate **2a** produced adduct **3a** in 75% isolated yield with complete suppression of competing acyl transfer pathways (Table 1, entry 5). A modest increase in temperature improved the isolated yield of **3a** to 86% (Table 1, entry 6). Variation in the loading of **2a** was explored under these conditions (Table 1, entries 6–8), and a loading of 300 mol% was deemed optimal (Table 1, entry 7). Further variation in ligand did not avail further improvement (Table 1, entries 9–11). In the absence of ligand, only trace quantities of **3a** were observed (Table 1, entry 12).

To assess the generality of this process with respect to the vinyl donor, ethyl mandelate **1a** was subjected to these optimal conditions in the presence of vinyl pivalates *O*-Piv-**2a-2f** (Table 2). Although the unsubstituted vinyl pivalate *O*-Piv-**2a** is an efficient partner for vinyl transfer, the use of more highly substituted vinyl pivalates *O*-Piv-**2b-2f** was less efficient due to competing *O*-acylation. The use of the corresponding triphenyl acetates *O*-TPA-**2b, 2c, 2f** suppresses transesterification, delivering the desired products of vinyl transfer **3b, 3c, 3f** in moderate to excellent yields (Table 2). *N*-Benzyl-3-hydroxy-2-oxindole **1b** was subjected to a parallel set of vinyl transfer experiments (Table 3). Dehydrogenation of **1b** gives rise to a highly reactive isatin that readily engages in oxidative coupling, allowing the parent ruthenium(0) catalysts to be employed and attenuating competitive transesterification that previously accompanied use of vinyl acetates. Nevertheless, in certain cases the vinyl pivalates are required to enforce better partitioning of *O*-acylation and C-C coupling pathways. For example, the enol acetates *O*-Ac-**2e** and *O*-Ac-**2f** fail to deliver the desired adducts **4e** and **4f**, respectively due to competing acyl transfer. In contrast, the corresponding vinyl pivalates *O*-Piv-**2e** and *O*-Piv-**2f** deliver adducts **4e** and **4f** in 94% and 90% yields, respectively. The yield of **4c** was increased from 60% to 85% by suppression of *O*-acylation when using triphenyl acetates *O*-TPA-**2c**. The conversion of 3-hydroxy-2-oxindole **1b** to adduct **4g** demonstrates the feasibility of transferring trisubstituted alkenes that are activated in the form of conjugated enones (eq.5). Finally, vinyl transfer can be

performed from the dicarbonyl oxidation level, as illustrated in the reductive coupling of *oxo-1b* with vinyl acetate **2a** (eq.6).

(eq. 5)

(eq. 6)

Vicinal diols, which can form 1,2-diketones as reactive intermediates, were explored as electrophilic partners in vinyl transfers using *O*-Piv-**2a**, *O*-TPA-**2d** and *O*-TPA-**2c** (Table 4). The reactions of vicinal diols **1c-1h** are oxidative and require excess vinyl donor as sacrificial hydrogen acceptor. It was found that aryl substituted 1,2-diols **1c-1g** react with *O*-Piv-**2a** engage in vinyl transfer to form adducts **5a-5e** in moderate to good yields. For non-symmetric diols **1c**, **1d**, **1f** and **1g**, the vinyl transfer proceeds in a completely regioselective manner and can be explained on the basis of our prior density functional theory (DFT) calculations in related alkyne-diol C-C couplings.¹³ The more highly substituted triphenyl acetate *O*-TPA-**2c** reacts with aryl substituted diols **1c**, **1d**, **1f** and **1g**, delivering adducts **6a**, **6b**, **6d** and **6e** in up to 93% isolated yield. Adduct **6c** was not formed presumably due to steric issues. Simple aliphatic diols, such as cyclohexane diol **1h**, participate in vinyl transfer, as illustrated in the formation of adducts **5f** and **6f**. Here, somewhat modest yields were observed due to competitive transesterification. Phenyl-(2-pyridyl)-methanol and related heteroaromatic secondary alcohols do not participate in vinyl transfer under the aforesaid conditions.

A plausible catalytic mechanism is illustrated for the coupling of ethyl mandelate **1a** with enol carboxylates **2** to form adducts **3** (Scheme 2). Prior mechanistic studies involving the use of $\text{Ru}_3(\text{CO})_{12}$ precatalysts^{9d} suggests intervention of a discrete mononuclear osmium(0) complex modified by XPhos. Osmium(0) mediated oxidative coupling *oxo-1a* with enol carboxylate **2** provides a transient β -carboxy-oxaosmacycle **I**. Related ruthenium(0) mediated carbonyl-alkene oxidative couplings find precedent in the work of Chatani and Murai¹⁰ and our own studies.^{9,13} The regioselectivity of oxidative coupling is likely driven by formation of a less hindered primary carbon-osmium bond. Reversible oxidative coupling, as demonstrated in a related system,^{9d} might correct errors in regioselectivity. The β -carboxy-oxaosmacycle **I** undergoes fragmentation to form the osmium(II) carboxylate

II,^{7j,k} which upon substitution by ethyl mandelate **1a** delivers the osmium(II) alkoxide complex **III**. The intermediate **III** undergoes β -hydride elimination to furnish the α -ketoester *oxo-1a* and the osmium(II) hydride **IV**, which upon O-H reductive elimination provides the product of vinyl transfer **3** to close the catalytic cycle.

In summary, we report a broad, new strategy for catalytic vinyl transfer from enol carboxylates to activated secondary alcohol C-H bonds *via* metallacycle fragmentation under the conditions of ruthenium(0) and osmium(0) catalyzed transfer hydrogenation. This method is applicable to a range of activated secondary alcohols and vicinal diols **1c-1h**. Future studies will focus on the development of related C-C bond forming transfer hydrogenations that directly convert lower alcohols to higher alcohols in the absence of stoichiometric organometallic reagents.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Prior Art: Vinyl Transfer *via* Carbonyl Addition, Reductive & Redox-Neutral Coupling **This Work:** Catalytic Vinyl Transfer *via* Metallacycle Fragmentation **Scheme 1.**

Convergent Methods for the Synthesis of Allylic Alcohols through Vinyl Transfer.

Scheme 2.
Proposed General Catalytic Mechanism Involving Oxidative Coupling-Metallacycle Fragmentation.

Selected Optimization Experiments in the Redox-Triggered C-H Vinylation of Ethyl Mandelate **1a**.^a

Table 1

Entry	2a (mol%)	M	Ligand	T (°C)	time (h)	3a:O-Ac/Piv-1a	
1	O-Ac-2a (500)	-	-	130	20	trace (0:1)	
2	O-Ac-2a (500)	-	XPhos	130	20	trace (0:1)	
3	O-Ac-2a (500)	Ru	XPhos	130	20	29(1:1)	
4	O-Ac-2a (500)	Os	XPhos	130	20	85(9.5:1)	
5	O-Piv-2a (500)	Os	XPhos	130	24	75 (>20:1)	
6	O-Piv-2a (500)	Os	XPhos	140	24	86 (>20:1)	
⇒ 7	O-Piv-2a (300)	Os	XPhos	140	24	83 (>20:1)	
8	O-Piv-2a (200)	Os	XPhos	140	24	76 (>20:1)	
9	O-Piv-2a (300)	Os	RuPhos	140	24	72 (>20:1)	
10	O-Piv-2a (300)	Os	PCy ₃	140	24	50 (>20:1)	
11	O-Piv-2a (300)	Os	PCy ₂ Ph	140	24	28 (>20:1)	
12	O-Piv-2a (300)	Os	-	140	24	trace (>20:1)

$\text{RuPhos, R}^1 = \text{O-}i\text{Pr, R}^2 = \text{H}$
 $\text{XPhos, R}^1 = \text{R}^2 = i\text{Pr}$

^aYields are of material isolated by silica gel chromatography. See Supporting Information for further experimental details.

Table 2Osmium Catalyzed Vinyl Transfer from Enol Carboxylates **2** to Ethyl Mandelate **1a** to Form **3a-3f**.^a

1a (100 mol%)	2a-2f , R ¹ = <i>t</i> Bu 2b-2f , R ¹ = CPh ₃ (300 mol%)	3a-3f
2a , R ² = H 2d , R ² = Ph	2b , R ² = Me 2e , R ² = 3,5-(CF ₃) ₂ Ph	2c , R ² = <i>c</i> -Pr 2f , R ² = benzodioxole

3a , 83% Yield (O-Piv)	3b , 53% Yield (O-Piv) 80% Yield (O-TPA)	3c , <i>not formed</i> (O-Piv) 65% Yield (O-TPA)

3d , 71% Yield (O-Piv)	3e , 80% Yield (O-Piv)	3f , 20% (O-Piv) 68% Yield (O-TPA) ^b

^a Yields are of material isolated by silica gel chromatography.^b Os₃(CO)₁₂ (4 mol%) and XPhos (24 mol%), isolated yield based on recovered starting material. See Supporting Information for further experimental details.

Table 3

Ruthenium Catalyzed Vinyl Transfer from Enol Carboxylates **2** to 3-Hydroxy Oxindole **1b** to Form **4a-4f**.^a

<p> $\text{Ru}_3(\text{CO})_{12}$ (2 mol%), XPhos (12 mol%), PhMe (2.0 M), 130 °C, 4-48 h </p> <p> 1b (100 mol%), 2 (300 mol%) </p> <p> O-Ac-2a, 2b, 2d-2f, $\text{R}^1 = \text{Me}$ O-Piv-2c, 2e, 2f, $\text{R}^1 = \text{tBu}$ O-TPA-2c, $\text{R}^1 = \text{CPh}_3$ </p> <p>4a-4f</p>		
2a , $\text{R}^2 = \text{H}$ 2d , $\text{R}^2 = \text{Ph}$	2b , $\text{R}^2 = \text{Me}$ 2e , $\text{R}^2 = 3,5\text{-(CF}_3)_2\text{Ph}$	2c , $\text{R}^2 = \text{c-Pr}$ 2f , $\text{R}^2 = \text{benzodioxole}$
<p>4a, 99% Yield (O-Ac)</p>	<p>4b, 85% Yield (O-Ac)</p>	<p>4c, 60% Yield (O-Piv) 85% Yield (O-TPA)</p>
<p>4d, 87% Yield (O-Ac)</p>	<p>4e, not formed (O-Ac) 94% Yield (O-Piv)</p>	<p>4f, not formed (O-Ac) 90% Yield (O-Piv)</p>

^aYields are of material isolated by silica gel chromatography. See Supporting Information for further experimental details.

Table 4

Osmium Catalyzed Vinyl Transfer from Enol Carboxylates **2** to 1,2-Diols **1c-1h** to Form **5a-5f** and **6a, 6b, 6d-6f**.^a

<div> <div> <p>1c-1h (100 mol%)</p> </div> <div> <p>O-Piv-2a, O-TPA-2d, O-TPA-2c (500 mol%)</p> </div> <div> <p>Os₃(CO)₁₂ (2 mol%) XPhos (12 mol%) PhMe (2.0 M) 130-150 °C 24-48 h</p> </div> <div> <p>5a-5f 6a, 6b, 6e-6f</p> </div> </div>
<div> <div> <p>1c, <i>trans</i>-indane-1,2-diol</p> <p>1e, <i>trans</i>-dihydroacenaphthylene-1,2-diol</p> <p>1g, <i>cis</i>-2,2-dimethylchroman-3,4-diol</p> </div> <div> <p>1d, <i>trans</i>-tetrahydronaphthalene-1,2-diol</p> <p>1f, <i>cis</i>-chroman-3,4-diol</p> <p>1h, <i>trans</i>-cyclohexane-1,2-diol</p> </div> </div>
<div> <div> <p>5a, 67% Yield (O-Piv, R² = H)</p> <p>6a, 71% Yield (O-TPA, R² = <i>c</i>-Pr)</p> </div> <div> <p>5b, 70% Yield (O-Piv, R²=H)</p> <p>6b, 70% Yield (O-TPA, R²=<i>c</i>-Pr)</p> </div> <div> <p>5c, 60% Yield (O-Piv, R²=H)</p> <p>6c, not formed (O-TPA, R²=<i>c</i>-Pr)</p> </div> </div>
<div> <div> <p>5d, 88% Yield (O-Piv, R²=H)</p> <p>6d, 93% Yield (O-TPA, R²=<i>c</i>-Pr)</p> </div> <div> <p>5e, 87% Yield (O-Piv, R²=H)</p> <p>6e, 82% Yield (O-TPA, R²=<i>c</i>-Pr)</p> </div> <div> <p>5f, 40% Yield (O-TPA, R²=Ph)</p> <p>6f, 65% Yield (O-TPA, R²=<i>c</i>-Pr)</p> </div> </div>

^aYields are of material isolated by silica gel chromatography. See Supporting Information for further experimental details.