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Contemporaneous Dual Catalysis by Coupling Highly Transient Nucleophilic and Electrophilic Intermediates Generated in Situ

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## Pd/V Contemporaneous Dual Catalysis

OH R1 
$$\rightarrow$$
 Parameters  $\rightarrow$  OBoc  $\rightarrow$  OV(OSiPh<sub>3</sub>)<sub>3</sub> (1.5 mol%), Pd<sub>2</sub>dba<sub>3</sub> CHCl<sub>3</sub> (0.5 mol%)  $\rightarrow$  R2  $\rightarrow$  R3 Substrate scope:

NHBoc  $\rightarrow$  Ph  $\rightarrow$  B2% yield ( $\rightarrow$  Ph  $\rightarrow$  B3% yield ( $\rightarrow$  Ph  $\rightarrow$  Ph  $\rightarrow$  B3% yield ( $\rightarrow$  Ph  $\rightarrow$  Ph  $\rightarrow$  B3% yield ( $\rightarrow$  Ph

**Significance:** The authors report a novel Pd/V dual catalysis process that couples propargyl alcohols and allyl carbonates to afford enones in moderate to excellent stereoselectivity. The authors define this reaction as 'contemporaneous dual catalysis' – a process in which two catalytically formed highly transient intermediates react chemoselectively in the presence of other stoichiometric reactive species. This is the first instance in which this type of reaction between two catalytically formed intermediates has been reported in the literature.

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**Comment:** The substrate scope of this transformation is quite broad wherein a variety of propargyl alcohols and allyl carbonates react to form enones in moderate to excellent yields and moderate to high stereoselectivities. Although the products themselves may be accessible through various alternate methods, this report provides an important proof-of-principle of contemporaneous dual catalysis. If two catalytically formed reactive intermediates can be intercepted efficiently and chemoselectively using a combination of catalyst systems, a multitude of chemical transformations may be accessible.

side-product (major with Pd only)

## Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

## Key words

contemporaneous dual catalysis

palladium

vanadium

α,β-unsaturated ketones

