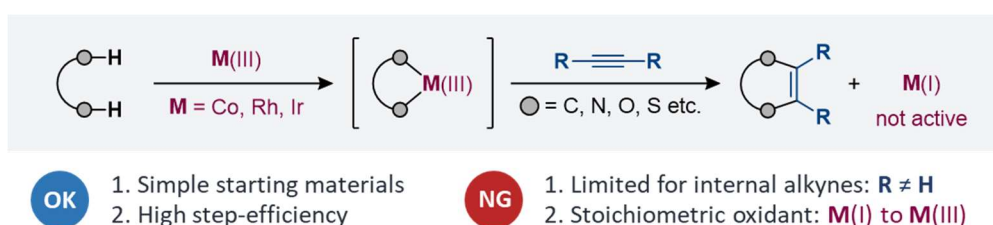


Catalytic Vinylene Transfer Reaction for the Direct Construction of Multi-Ring Systems

(Graduate School of Engineering, Osaka University) ○Yuji Nishii

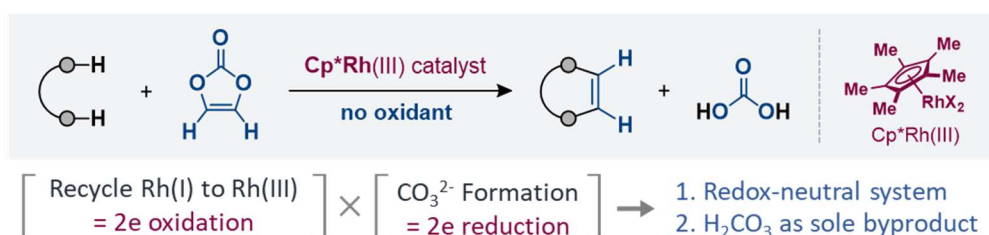
Keywords: C-H Activation, Rhodium, Acetylene, Vinylene Carbonate

Transition-metal-catalyzed C–H activation and subsequent oxidative annulation with alkynes or their equivalents have emerged as promising synthetic tools for the assembly of heterocycles.¹ This method allows us to construct various fused-ring systems with simple manipulations; however, most of these reactions are only applicable to internal alkynes. This limitation significantly takes from the practical value of the annulative coupling reaction because a non-substituted vinylene fragment cannot be installed via the catalysis.^{1e} Moreover, a stoichiometric amount of external oxidant is usually required to ensure the catalytic turnover, leading to the formation of undesired byproducts (Scheme 1).



Scheme 1. Schematic Representation of the Catalytic Oxidative Annulation

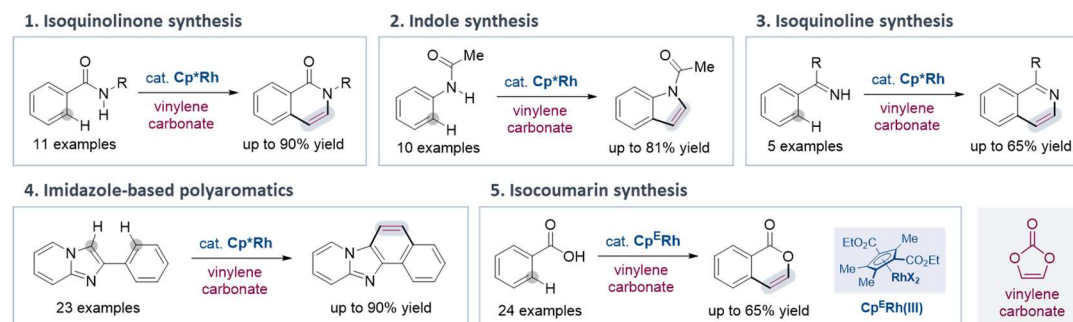
To address this issue, we envisioned using vinylene carbonate as an oxidizing acetylene surrogate.² Vinylene carbonate is a bench-stable reagent with bulk production as an electrolyte and for polymer chemistry. Upon liberation of the $[CO_3]^{2-}$ anion (formal two-electron reduction), vinylene carbonate might act as a two-electron internal oxidant under proper reaction conditions to establish a redox-neutral reaction system (Scheme 2). Overall, only H_2CO_3 (or $H_2O + CO_2$) would form as a byproduct.



Scheme 2. A Working Hypothesis for the Catalytic Vinylene Transfer Reaction

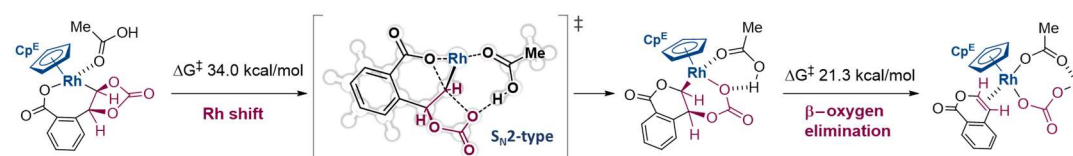
With this picture in mind, we investigated the annulative coupling using vinylene carbonate as a coupling partner and, to our delight, a standard $Cp^*Rh(III)$ catalyst produced favorable outcomes. Various nonsubstituted vinylene-fused N-heteroaromatic compounds

involving isoquinolones, indoles, benzimidazoles, isoquinolines, and benzothiazines were directly synthesized through the C–H/N–H oxidative cyclization.^{3a} Afterward, C–H/C–H annulation with imidazole derivatives^{3b} as well as C–H/O–H annulation with benzoic acids^{3c} were found to be feasible (Scheme 3).



Scheme 3. Examples of the Oxidative Annulation with Vinylene Carbonate

In order to gain insight into the mechanism of this vinylene transfer protocol, we conducted a computational study. A concerted S_N2 -type reaction was thus proposed to support the redox-neutral system (Scheme 4).^{3c} The detailed discussion on the mechanism and some synthetic applications would be introduced in this presentation.



Scheme 4. DFT Calculation for the Proposed Reaction Mechanism

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