Discussion Addendum for:
Iridium-catalyzed Synthesis of Vinyl Ethers from Alcohols and Vinyl Acetate

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The synthesis of vinyl ethers by vinyl transfer from vinyl esters to alcohols constitutes the basis for much useful methodology. The originally reported iridium-catalyzed process provides a versatile and practical route to access vinyl alcohols.2 This methodology was successfully expanded to facilitate allyl transfer from allyl acetates to alkyl alcohols, providing allyl ethers as products.3 In addition, as a successful application of this protocol, the one-pot synthesis of γ,δ-unsaturated carbonyl compounds from allyl alcohols and vinyl acetates was achieved through in situ iridium-catalyzed formation of allylic vinyl ethers followed by Claisen rearrangement.4 The above-mentioned advances will be summarized here.

Scope of Allylation of Alcohols from Allyl Acetates

Vinyl ethers and allyl ethers are important classes of compounds that have been used in polymer synthesis and in the pharmaceutical chemistry,5 as well as starting materials for Claisen rearrangements,6 cycloadditions,7 hydroformylations,8 and Mizoroki-Heck reactions,9 etc.

We found that the iridium cationic complex [Ir(cod)2]BF4 catalyzed the allylation of alcohols with allyl acetate to afford allyl ethers as products.3 For instance, the reaction of allyl acetate with n-octyl alcohol in the presence of a catalytic amount of [Ir(cod)2]BF4 complex afforded allyl octyl ether in quantitative yield (Figure 1).
Figure 1. Ir-catalyzed reaction of \( n \)-octyl alcohol with allyl acetate to allyl octyl ether

**Application of the Vinyl Transfer Methodology in Organic Synthesis**

We previously reported the rearrangement of allyl homoallyl ethers to \( \gamma,\delta \)-unsaturated aldehydes induced by the \([\text{IrCl(cod)}]_2\) complex.\(^{10}\) Therefore, this protocol would serve as a useful route for the formation of \( \gamma,\delta \)-unsaturated carbonyl compounds from allyl alcohols with vinyl or isopropenyl acetate through the formation of vinyl ethers as the key intermediate.\(^4\) For example, the reaction of \textit{trans}-2-methyl-3-phenyl-2-propen-1-ol with isopropenyl acetate in the presence of \([\text{IrCl(cod)}]_2\) catalyst combined with \( \text{Cs}_2\text{CO}_3\) at 100 °C for 3 h followed by heating at 140 °C for 15 h afforded 5-methyl-4-phenyl-5-hexen-2-one in 83% yield (Figure 5). The reaction is thought to proceed through the Claisen rearrangement of the in situ generated allylic vinyl ether.

Figure 2. Ir-catalyzed one-pot synthesis of \( \gamma,\delta \)-unsaturated carbonyl compounds
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