

Allylic Alcohols as Substrate for Ruthenium-Catalyzed C–C Coupling Allylation Reactions

Preliminary Communication

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Allylic alcohols, rather than halides, acetates, or carbonates can be used directly in the *Friedel–Crafts*-type coupling with various phenols. The use of a Ru^{IV}, rather than a Ru^{II}, precursor promotes the formation of one H⁺ per cycle so that a large excess of acid is never present in the reaction mixture. Consequently, the leaving group in the oxidative addition reaction is H₂O, thereby avoiding the production of an unnecessary by-product.

An increasing variety of metal-mediated catalytic transformations involving allyl compounds have been developed, and these tools are rapidly becoming indispensable in organic synthesis [1–5]. Generally, π - or σ -allyl species are regarded as important intermediates in these various transformations [6][7]. Typically, allyl sources such as halides, acetates, or carbonates have been employed since the allyl moiety often requires a ‘leaving group’ to be effective; however, the direct activation of an allyl alcohol is both economically and environmentally more desirable, in that the leaving group is not wasted.

One finds only a modest number of reports in which an allyl alcohol is employed as substrate [8–13], and *Akita* and co-workers [8] have summarized several mechanistic possibilities for the use of an alcohol, *e.g.*, either an oxidative addition reaction or a dehydration pathway. The former is not favored because the OH group is thought to be a poor leaving group. The latter mechanism works under acidic conditions; however, this often requires excess acid and/or severe reaction conditions [8].

We have recently shown [14] that [Ru(Cp*)(MeCN)₂](η^3 -PhCH=CHCH₂)](PF₆)₂ ((Cp* = 1,2,3,4,5-pentamethylcyclopenta-1,3-dien-1-yl); **1**) facilitates *Friedel–Crafts* type aromatic allylation reactions of phenols and related arene compounds under relatively mild conditions, using allyl carbonate substrates. There is now a modest literature involving metal-catalyzed *Friedel–Crafts* reactions [15], but little involving ruthenium [16]. We report here an extension of this chemistry and show that the dicationic catalyst precursor **1**, which contains Ru^{IV} rather than Ru^{II}, affords the C–C coupling products starting from a selection of alcohols, as indicated in *Scheme 1*. The *Table* gives a list of the substrates and products tested. The reactions were, in many cases, fairly rapid (often complete conversion in less than 20 min) and regioselective in that the attack occurred at the least-substituted allyl C-atom, and proceeded to completion under relatively mild conditions in MeCN solution. Several of the tested alcohols