Decarbonylative Coupling

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Ruthenium-Catalyzed Alkene Synthesis by the Decarbonylative Coupling of Aldehydes with Alkynes

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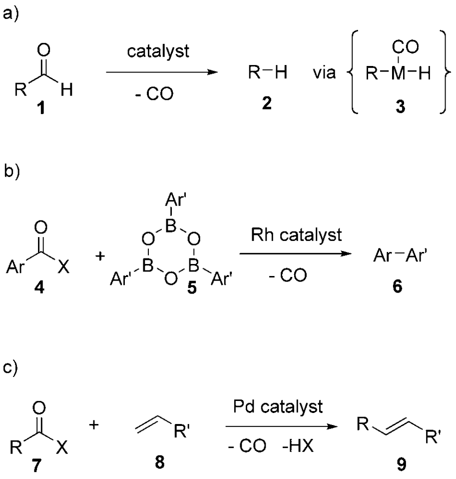
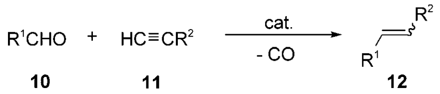
The decarbonylation of aldehydes using $[Rh(PPh_3)_3Cl]$ was first reported in 1965, originally using stoichiometric amounts of the metal.[1] There are now many examples of catalytic variants of the decarbonylation of an aldehyde **1** to give the decarbonylated product **2** (Scheme 1 a). Recent examples include the use of $RhCl_3{\cdot}3H_2O$ with $Ph_2PCH_2CH_2CH_2PPh_2$ in diglyme at reflux[2] and $[\{Ir(cod)Cl\}_2]$ with PPh_3 in dioxane at reflux.[3] These reactions are believed to proceed by oxidative addition of the catalyst into the C–H bond of the aldehyde and fragmentation of the acyl group to give intermediate **3**. Reductive elimination of R–H and dissociation of CO completes the catalytic cycle. Ruthenium catalysts have also been used for the decarbonylation of aldehydes,[4] and in some cases the decarbonylation process has been used as a convenient source of carbon monoxide for Pauson–Khand reactions with rhodium, iridium, and ruthenium catalysts.[5] There have been synthetically important developments that involve the use of suitable acyl substrates, including acid anhydrides **4** (X = OCOAr) and isopropenyl esters **7** (X = OC(Me)=CH$_2$), which undergo decarbonylation and subsequent coupling.[6] Examples include the decarbonylative Suzuki reaction (Scheme 1 b)[7] and the decarbonylative Heck reaction (Scheme 1 c).[8] The palladium-catalyzed decarbonylation of carboxylic acid derivatives to give alkenes is also known.[9]



Scheme 1. Metal-catalyzed reactions involving the loss of CO. a) Decarbonylation of aldehydes. b) Decarbonylative Suzuki reaction. c) Decarbonylative Heck reaction.

Li and co-workers recently reported a ruthenium-catalyzed alkene synthesis, which they describe as a decarbonylative addition reaction, coupling an aldehyde **10** and an alkyne **11** with loss of carbon monoxide to form an alkene **12** (Scheme 2).[10] The process contrasts with hydroacylation reactions in which the carbonyl group is retained.[11] The only previous report of an intermolecular decarbonylative addition to alkynes involves the use of acylstannanes to give vinylstannane products catalyzed by Pd/C.[12]



Scheme 2. Decarbonylative addition of aldehydes to terminal alkynes.

After a thorough screening of catalyst combinations, the reported system of 10 mol % $[\{Ru(cod)Cl_2\}_n]$, 30 mol % $CuCl_2{\cdot}2H_2O$, and five equivalents LiCl was found to give the best conversions. The presence of water provided by $CuCl_2{\cdot}2H_2O$ was found to be beneficial, and the authors speculate that the chloride ion helps to stabilize the catalyst. A range of alkenes was synthesized using this methodology, including the decarbonylative addition of *p*-methoxybenzaldehyde to either 1-decyne or phenylacetylene to generate the alkenes **13** and **14**. In another example, piperonal was converted into alkene **15** by decarbonylative addition to a fluoro-substituted phenylacetylene. Noteworthy is the fact that cinnamaldehyde could also be used as a substrate, yielding the 1,3-butadiene product **16**. All products show an excess of the *E* alkene, and the exact ratio varies with the substrate (Scheme 3).

Despite these promising results, there are some limitations to the range of suitable substrates. Aliphatic aldehydes as well as internal alkynes fail to react under the present

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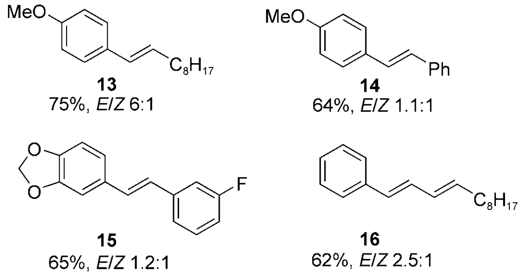
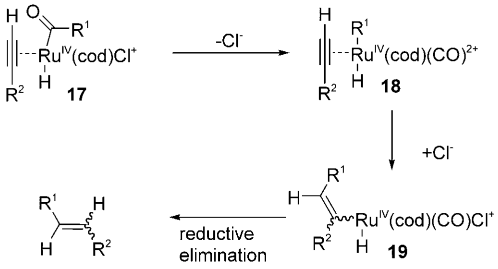


Scheme 3. Representative alkenes formed by decarbonylative addition to alkynes.

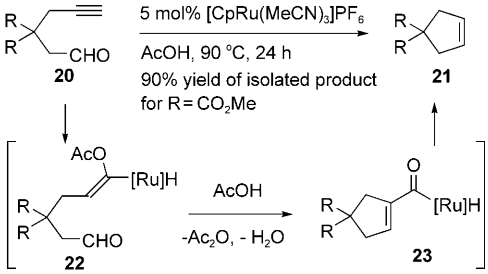
conditions (although aliphatic alkynes are suitable), and aldehydes containing electron-withdrawing substituents on the phenyl ring saw a considerable reduction in yield compared with those containing electron-donating groups.

The authors have tentatively proposed a mechanism with complexation of the ruthenium catalyst to the alkyne and subsequent oxidative addition to generate the Ru^{IV} complex **17**. Decarbonylation of the aldehyde leads to complex **18**, and addition across the alkyne triple bond gives complex **19**, which undergoes reductive elimination to generate the alkene product (Scheme 4). Further mechanistic work will need to be undertaken to confirm the involvement of Ru^{IV} intermediates and the order of the decarbonylation step in the catalytic sequence.



Scheme 4. Mechanistic proposal.

It is interesting to compare the work of Li with an earlier report from Saá and co-workers, who described the ruthenium-catalyzed cyclization of terminal alkynals **20** into cycloalkenes **21** in the presence of acetic acid (Scheme 5).[13] They suggested that the carbon atom lost during the decarbonylation step is the terminal carbon atom of the alkyne and that an initial C–H insertion into the aldehyde is unlikely. They propose that the reaction proceeds by initial formation of a Ru^{II} vinylidene species, with addition of acetic acid generating complex **22**, which undergoes an intramolecular cyclization akin to an aldol condensation. Subsequent decarbonylation of intermediate **23** leads to cyclic alkene **21**. This mechanism is supported by the fact that they subsequently reported a decarbonylative cyclization of 1,6-diynes in which there is no aldehyde present in the starting material, and the CO is again believed to arise from loss of the terminal carbon atom of the alkyne.[14] Suitable ^{13}C labeling studies are probably required to establish unambiguously which carbon atom is lost in the Li group's work.



Scheme 5. Intramolecular cyclization of alkynals. Cp = C_5H_5.

In summary, Li and co-workers have reported the first examples of an intermolecular decarbonylative addition of aldehydes to alkynes to give alkenes. This work makes an important addition to the range of useful ruthenium-catalyzed reactions involving alkynes, and further developments to lower the catalyst loading, enhance control of *E*/*Z* selectivity, and increase the substrate scope will be welcomed, especially if alkenes can also be used as substrates.

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