

## Ruthenium Catalysed Synthesis of Unsaturated Acetals and Aldehydes via C–C Bond Coupling of Alkynes with Allyl Alcohol

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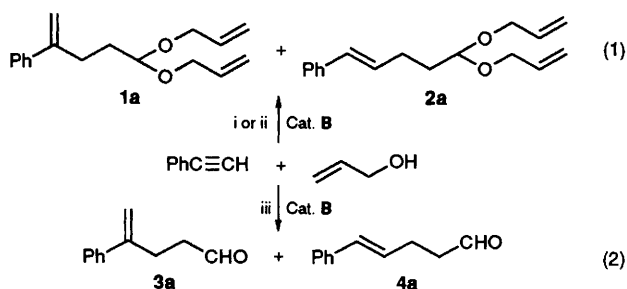
Terminal alkynes and allyl alcohol are coupled, with carbon–carbon bond formation, in the presence of a Ru<sup>IV</sup>(C<sub>5</sub>Me<sub>5</sub>) catalyst, to give  $\gamma,\delta$ -unsaturated acetals and with  $[\{\text{RuCl}(\text{C}_5\text{Me}_5)_4\}]$  or  $[\text{RuCl}(\text{cod})(\text{C}_5\text{Me}_5)]$  preferentially to produce the branched  $\gamma,\delta$ -unsaturated aldehydes.

The selective catalytic coupling of simple substrates, *via* C–C bond formation, is a problem of current interest, either for the discovery of new reaction pathways or for access to reactive intermediates,<sup>1,2</sup> and provides impetus to the search for new applications of metal complexes. Recently, the use of ruthenium catalysts for organic synthesis has led to the discovery of selective transformations of alkynes<sup>3,4</sup> and carbon–carbon bond forming processes. Representative examples of the latter deal with the dimerization of alkynes affording enynes<sup>5</sup> or butatriene,<sup>6</sup> the carbonylation of diynes to give phenols,<sup>7</sup> the coupling of allylic alcohols with terminal alkynes, *via* ruthenium–vinylidene<sup>8</sup> or ruthenium–allenylidene<sup>9</sup> intermediates, to afford  $\alpha,\beta$ -unsaturated ketones, and the codimerization of alkynes with olefins selectively to produce cyclobutenes,<sup>10</sup> dienes<sup>11,12</sup> or  $\gamma,\delta$ -unsaturated ketones<sup>13</sup> and but-enolides.<sup>14</sup>

We report here the one-step synthesis of unsaturated acetals and aldehydes *via* coupling of alkynes with allyl alcohol and a comparative study of ruthenium(IV) and ruthenium(II) catalyst precursors containing the Ru(C<sub>5</sub>Me<sub>5</sub>) moiety; we show that the Ru(C<sub>5</sub>Me<sub>5</sub>) moiety favours the formation of branched aldehydes.

The reaction of phenylacetylene in neat allyl alcohol, in the presence of the catalyst  $[\text{RuCl}_2(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{C}_5\text{H}_5)]$ <sup>15</sup> **A** led only to 20% of conversion of the alkyne after 22 h at 90 °C and afforded a mixture of unsaturated acetals **1a/2a** (33/67) in low yield. When the same reaction was performed in the presence of  $[\text{RuCl}_2(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{C}_5\text{Me}_5)]$ <sup>15</sup> **B**, phenylacetylene was totally converted after 4 h at 90 °C with opposite regioselectivity in C–C bond formation. Products **1a/2a** (67/33) were obtained in 60% yield (Scheme 1). In an allyl alcohol–water (1:4) mixture, the same reaction in the presence of catalyst **B** directly afforded the aldehydes **3a/4a** (68/32) isolated in 58% yield.

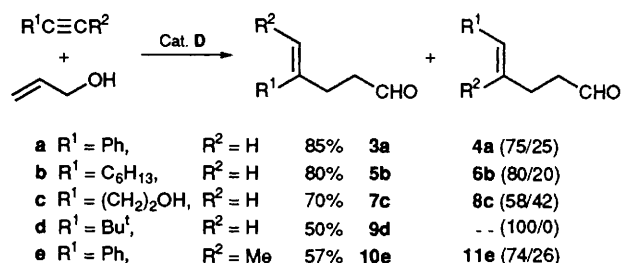
Thus the replacement of the C<sub>5</sub>H<sub>5</sub> ligand in **A** by the bulkier, more electron-releasing C<sub>5</sub>Me<sub>5</sub> group in **B** significantly increases the activity of the ruthenium(IV) catalyst and reverses the regioselectivity of the C–C bond formation preferentially to give the branched unsaturated derivative. The nature of the major branched compounds **1a** and **3a** shows



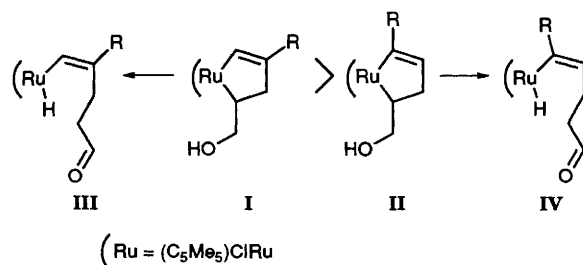
**Scheme 1** General conditions at 90 °C: i, phenylacetylene (2.5 mmol), allyl alcohol (5 ml),  $[\text{RuCl}_2(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{C}_5\text{H}_5)]$  **A** (0.125 mmol), 22 h; ii, as for i, except catalyst  $[\text{RuCl}_2(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{C}_5\text{Me}_5)]$  **B** (0.125 mmol), 4 h; iii, as for ii, except allyl alcohol (1 ml), water (4 ml)

that the catalyst **B** does not activate the phenylacetylene *via* a ruthenium vinylidene intermediate, giving addition of the alcohol to C(1).<sup>8</sup> It rather suggests that the reaction results from oxidative coupling of the C≡CH and CH<sub>2</sub>=CH bonds at the ruthenium site and, consequently, it is likely that the ruthenium(IV) complex **B** releases *in situ*, by loss of allyl chloride, a coordinatively unsaturated ruthenium(II) catalytic species  $[\text{RuCl}(\text{C}_5\text{Me}_5)]$  more able to lead to an oxidative coupling. This hypothesis led us to test ruthenium(II) catalysts containing the C<sub>5</sub>Me<sub>5</sub> ligand.

$[\{\text{RuCl}(\text{C}_5\text{Me}_5)_4\}]$  **C**, under the reaction conditions of eqn. (2) (Scheme 1), afforded **3a/4a** in a similar ratio and yield as catalyst **B**. However,  $[\text{RuCl}(\text{cod})(\text{C}_5\text{Me}_5)]$  **D**, obtained by addition of cycloocta-1,5-diene (cod) to **C**,<sup>16</sup> appeared to be the most efficient catalyst for the alkyne–allyl alcohol coupling reaction in terms of both activity and regioselectivity. Complex **D** (0.05 mol equiv.) allows the coupling of phenylacetylene with allyl alcohol to give, in the absence of water, directly the unsaturated aldehydes **3a/4a** (75/25) in 70% yield after 1 h at 90 °C, without the formation of acetals. In the presence of water, the yield of aldehydes increased to 85% (**3a/4a**: 75/25). Similarly oct-1-yne (**b**) and but-3-yn-1-ol (**c**) in allyl alcohol–water (1:8) led to the formation of **5b/6b** (80/20) and **7c/8c** (58/42) in 80 and 70% yields, respectively (Scheme 2). From 3,3-dimethylbut-1-yne (**d**) only the branched isomer **9d** was obtained (50%). The observed regioselectivity contrasts with that provided by  $[\text{RuCl}(\text{cod})(\text{C}_5\text{H}_5)]$  which favoured the linear coupling of terminal alkynes with secondary allylic alcohols.<sup>13</sup> The reaction is not specific of terminal alkynes, as expected for an oxidative coupling mechanism. Although the reaction is slower, 1-phenylprop-1-yne (**e**) is coupled with allyl



**Scheme 2** Conditions: alkyne (2.5 mmol), allyl alcohol (0.5 ml, 7.5 mmol), water (4 ml),  $[\text{RuCl}(\text{cod})(\text{C}_5\text{Me}_5)]$  **D** (0.125 mmol), 90 °C, 1 h



**Scheme 3**

alcohol in the presence of **D** to give both regioisomers **10e/11e** (74/26) in 57% yield.

The reaction is likely to proceed *via* the oxidative coupling intermediates **I** and **II**, prior to  $\beta$ -elimination **III** and **IV** and reductive elimination to give branched or linear aldehydes, respectively (Scheme 3). This scheme accounts for the greater activity of the electron-rich Ru<sup>II</sup>(C<sub>5</sub>Me<sub>5</sub>) precursor **D** towards oxidative coupling of hydrocarbons, compared with that of Ru<sup>IV</sup>(C<sub>5</sub>Me<sub>5</sub>) **B**. The steric hindrance of the C<sub>5</sub>Me<sub>5</sub> ligand favours the intermediate **I** rather than **II**, the regioselectivity being opposite with the Ru(C<sub>5</sub>H<sub>5</sub>) precursor **A**. The bulk of the Bu<sup>t</sup> group also favours intermediate **I** as only the aldehyde **9d** was observed. The interaction of the allyl alcohol hydroxy group with the ruthenium atom might account for the selective coupling of the unsubstituted carbon of the allyl alcohol. It is likely that the  $\beta$ -elimination involving the CH<sub>2</sub>OH group, giving the aldehyde, is easier than that involving the C(3)H<sub>2</sub> group in the metallocycle which would lead to the conjugated diene.

The efficiency of catalyst **D** is probably due to both the lability of the cod ligand, already observed recently with [RuCl(cod)(C<sub>5</sub>H<sub>5</sub>)],<sup>12</sup> and the electron-releasing effect of the C<sub>5</sub>Me<sub>5</sub> ligand. In fact, the complex **D** has recently been used as a catalyst for the [2 + 2] cycloaddition of norbornenes with alkynes.<sup>10</sup> It is noteworthy that, even if the ruthenium(IV) catalyst **B** is not as efficient as **D**, it appears to be a good catalyst for transformation of aldehydes into their acetals.

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