

Ruthenium Complex-catalysed Highly Selective Codimerisation of Acetylenes and Alkenes

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2,4-Dienes are prepared in high yields with high regioselectivity by the codimerisation of acetylenes and alkenes in the presence of a catalytic amount of Ru(cod)(cot) at 80 °C; cod = cycloocta-1,5-diene, cot = cycloocta-1,3,5-triene.

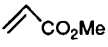
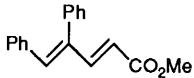
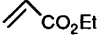
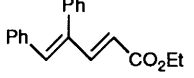
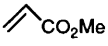
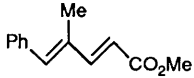

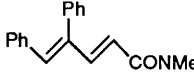

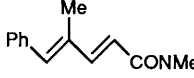

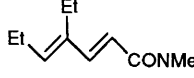


Recently, ruthenium complex-catalysed carbon-carbon bond forming reactions have been developed.¹ We have reported the efficient [2 + 2] cross-cycloaddition of acetylenes and norbornene catalysed by RuH₂(PBU₃)₄ or Ru(cod)(cot)-PBU₃² and the linear codimerisation of terminal acetylenes and 1,3-dienes catalysed by trialkylphosphine ruthenium complexes.³ We now report the selective linear codimerisation in the presence of a catalyst of acetylenes and alkenes with an electron-attracting group to give 2,4-dienes in high yields (Scheme 1). A representative procedure is as follows; to a mixture of Ru(cod)(cot) (0.2 mmol) and diphenylacetylene (5 mmol) under argon was added pyridine (20 mmol) and methyl acrylate (10 mmol). The mixture was stirred at 80 °C for

10 h. Kugelrohr distillation afforded 1.7 g (86%) of methyl (2*E*,4*Z*)-4,5-diphenylpenta-2,4-dienoate. This stereochemistry of the alkene was determined by means of nuclear Overhauser effect experiments for H^b on irradiating H^c (for the position of the proton, see Scheme 1).

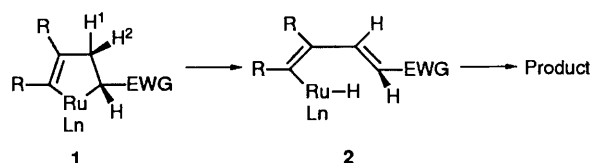
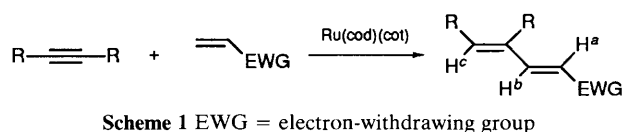
Representative results are shown in Table 1. The reaction of diphenylacetylene with ethyl acrylate gave ethyl (2*E*,4*Z*)-4,5-diphenylpenta-2,4-dienoate in 93% yield. Ru(cod)(cot) is the best catalyst in this reaction. Ru₃(CO)₁₂ and RuCl₃·3H₂O in pyridine showed no catalytic activity. The best yield was obtained in pyridine, while in triethylamine, toluene and tri-*n*-butylamine as solvent, the yields were low.

In the reaction of diphenylacetylene with *N,N*-dimethyl-

Table 1 Ru(cod)(cot)-catalysed codimerisation of acetylenes and alkenes^a

Run	Acetylene	Alkene	Conditions ^b	Reaction time / h	Product	Yield / %
1	PhC≡CPh		A	20		87
2	PhC≡CPh		A	20		93
3	PhC≡CMe		A	20		15 ^c
4	PhC≡CPh		B	0.25		81
5	PhC≡CMe		B	1		87
6	EiC≡CEi		B	9		54
7	Bu ^t C≡CH		B	9		25

^a Alkene (10 mmol), acetylene (5 mmol); Ru(cod)(cot) (cod = cycloocta-1,5-diene; cot = cycloocta-1,3,5-triene; 0.2 mmol), 80 °C under Ar.
^b A: pyridine (20 mmol); B: Alkene (10–20 mmol), without solvent. ^c Determined by GLC.



acrylamide, however, pyridine was not necessary. This reaction proceeded without solvent; in pyridine the yield was very low (7%). Methylphenylacetylene reacted with methyl acrylate to give the corresponding product in poor yield (7%), but it reacted with *N,N*-dimethylacrylamide to afford (*2E,4Z*)-*N,N*-dimethyl-4-methyl-5-phenylpenta-2,4-dienamide in 87% yield with complete regioselectivity. Diethylacetylene did not react with methyl acrylate, while it reacted with *N,N*-dimethylacrylamide to give *N,N*-dimethyl-(*2E,4E*)-4-ethylhepta-2,4-dienamide in 54% yield.

These results indicate that the Ru(cod)(cot)-catalysed codimerisation of acetylenes and alkenes is strongly affected by the solvent, ligand and the substituents on the acetylenes or alkenes.

Taking into account the mechanism of the [2 + 2] cycloaddition of norbornenes and dimethyl acetylenedicarboxylate, which is rationalised to proceed via a ruthenacyclopentene complex,² one of the plausible mechanisms is as follows.

Coordination of an acetylene and an alkene to a zero-valent ruthenium complex may give a ruthenacyclopentene complex **1** followed by the β -elimination of the β -hydrogen H¹ or H² and successive reductive elimination would give the product (Scheme 2).[†]

Although several linear cooligomerisations of alkenes and acetylenes are known,⁴ to our knowledge, this is the first example of an efficient catalytic linear codimerisation of acetylenes and alkenes to produce conjugated dienes.

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[†] The following two mechanisms cannot be ruled out completely. (i) Successive insertion of acetylene and alkene into a ruthenium-hydride bond followed by β -elimination. (ii) Oxidative addition of the sp²C-H bond of the alkene to ruthenium(0) complex followed by the insertion of acetylene and reductive elimination.