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Ruthenium complex-catalyzed coupling of vinyl halides with olefins

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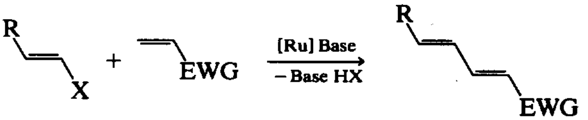
Abstract

Ruthenium complexes such as Ru(COD)(COT) [COD = cyclooctadiene, COT = cyclooctatriene], catalyze the dehydrohalogenative coupling of vinyl halides with olefins to give the corresponding substituted dienes. Even the sp^2-carbon–chloride bond of β-chlorostyrene is activated by ruthenium catalysts.

Introduction

Recently, characteristic ruthenium complex-catalyzed carbon–carbon bond forming reactions have been developed. Examples include co-oligomerization of olefins and/or acetylenes [1], (2 + 2) cross addition of norbornenes with acetylenes [2], addition of formyl compounds to olefins [3] and aldol condensation [4] and Michael addition reactions [4]. With respect to the reaction of organic halides, methylation of bromostyrene by methyl Grignard reagents [5], addition of polyhalides to olefins [6], and reactions of alkenyl sulfonyl chlorides with alkenes to give 1,3-dienes [7] have been reported. The last two reactions are catalyzed by $RuCl_2(PPh_3)_3$ and it has been suggested that these two reactions proceed via radical intermediates in the coordination sphere [6,7]. That ruthenium complex catalyzes dehydrohalogenative coupling of halides with olefins (eq. 1) has not previously been reported, though palladium complexes are well known to catalyze such reactions [8].

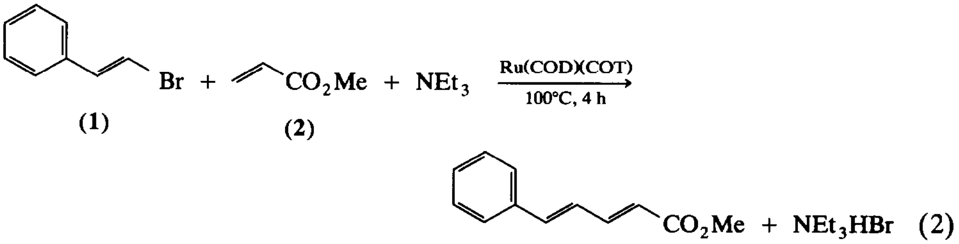


(1)

In the course of our study on carbon–carbon bond forming reactions catalyzed by low valent ruthenium complexes [1c], we have found that ruthenium complexes catalyze the reaction shown in eq. 1, and that in some cases ruthenium complexes are more active than palladium; we now report the results of the reaction.

Results and discussion

Vinyl halides with an aromatic group at β-carbon readily reacted with activated olefins in the presence of a catalytic amount of ruthenium complexes to give the corresponding dehydrohalogenative coupling products, conjugated dienes, in high yields (eq. 1). Representative results are summarized in Table 1. (*E*)-β-Bromostyrene reacted readily with methyl acrylate in the presence of a catalytic amount of Ru(COD)(COT) (COD = cyclooctadiene, COT = cyclooctatriene) (2 mol%) in NEt_3 at 100°C for 4 h to give the corresponding dehydrohalogenative coupling product, methyl (*E*,*E*)-5-phenyl-2,4-pentadienoate, in 68% yield (run 1). Use of an excess amount of methyl acrylate improved the yield of the product to 79% (eq. 2, run 2).



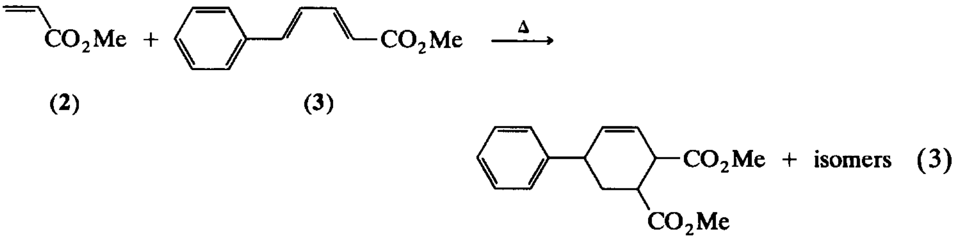
(1) (2)

(3, 79%)

(2)

2-Methyl-2-propenoate also gave the corresponding condensation product, methyl 2-methyl-5-phenylpentadienoate in 20% yield which was obtained as a mixture of stereoisomers [(2*E*,4*E*)/(2*Z*,4*E*) = 75/25, run 3]. *N*,*N*-Dimethylacrylamide similarly reacted with (*E*)-β-bromostyrene to give (*E*,*E*)-*N*,*N*-dimethyl-5-phenyl-2,4-pentadienamide in 70% yield (run 4). Methyl vinyl ketone also gave the corresponding diene, (*E*,*E*)-6-phenyl-3,5-hexadiene-2-one in 59% yield (run 5). When (*Z*)-β-bromostyrene was used as a starting material, the stereochemistry of the starting material could not be retained completely in the product; the (2*E*,4*E*)/(2*E*,4*Z*) ratio of the product was 66/34 (run 6). Methyl (*E*)-3-bromo-2-methylpropenoate also reacted with methyl acrylate to give dimethyl 5-methyl-2,4-hexadienedioate in 25% yield as a mixture of stereoisomers [(2*E*,4*E*)/(2*Z*,4*E*) = 50/50, run 7]. Addition of an excess amount of methyl acrylate did not improve the yield; all that was obtained was a tarry compound.

The optimum temperature for the reaction of β-bromostyrene with methyl acrylate was 100°C. At 120°C, the product, the diene 3, reacted with another mole of methyl acrylate to give a mixture of a number of Diels–Alder adducts, the formation of which decreased the yield of 3 (eq. 3). The product contained more than seven isomers and further identification was not performed.



(2) (3)

(4)

(3)

Table 1

Ru-catalyzed reactions of vinyl halides with olefins [a]

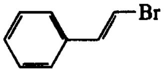
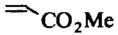
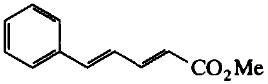
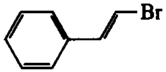
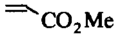
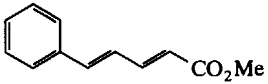
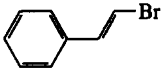
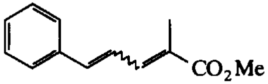
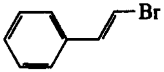
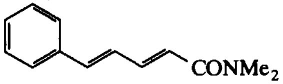
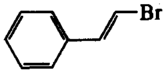
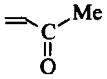
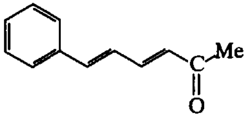
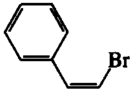
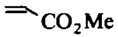
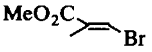
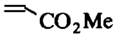
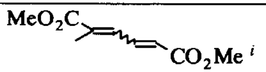
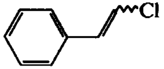
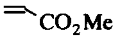
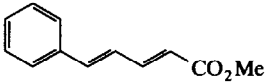
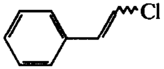
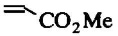
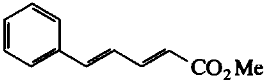
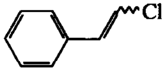
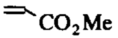
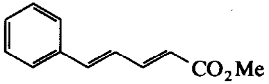
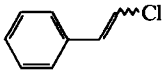
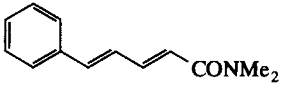
Run	Vinyl halide	Olefin	Catalyst	Time (h)	Conv. (%) [b]	Product	Yield (%) [c]
1			Ru(COD)(COT)	4	96		68
2		 [d]	Ru(COD)(COT)	4	98		79
3			Ru(COD)(COT)	21	-	 [g]	20
4			Ru(COD)(COT)	10	-		70
5			Ru(COD)(COT)	24	100		59
6			Ru(COD)(COT)	6	100	 [h]	51

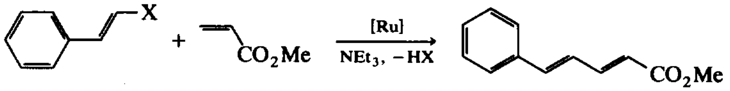
Table 1 (continued)

Run	Vinyl halide	Olefin	Catalyst	Time (h)	Conv. (%) [b]	Product	Yield (%) [c]
7			Ru(COD)(COT)	5	-	 [i]	25
8			Ru(COD)(COT)	22	35		28
9			Ru(COD)(COT) [e] /P(*p*-PhF)$_3$	13	55		40
10 [f]			Ru(COD)(COT) [e] /P(*p*-PhF)$_3$	18	60		43
11			Ru(COD)(COT)	10	-		51

[a] Reactions were carried out in a sealed tube with 5 mmol of vinyl halide, 10 mmol of olefin, 10 mmol of triethylamine and 0.1 mmol of catalyst at 100°C. [b] Conversions of vinyl halide determined by GLC. [c] Isolated yields based on the amount of vinyl halides used. [d] 50 mmol of olefin was used. [e] 10 mol% of the catalyst and the phosphine was used. [f] N-Methylpiperidine was used in place of triethylamine. [g] (2*E*,4*E*)/(2*Z*,4*E*) = 75/25. [h] (2*E*,4*E*)/(2*E*,4*Z*) = 66/34. [i] (2*E*,4*E*)/(2*Z*,4*E*) = 50/50.

Table 2

Ru-catalyzed reactions of β-halostyrene with methyl acrylate—activities of various catalysts [a]



	Catalyst	Yield of diene 3 (%) [b]	
		X = Br	X = Cl
1	Ru(COD)(COT)	68	28
2	$RuCl_3 \cdot nH_2O$	68	26
3	Ru(COD)(COT)/P(p-FC_6H_4)$_3$	34	40
4 [c]	$[RuCl_2(C_6Me_6)]_2/Na_2CO_3$/EtOH	57	45
5	$Ru_3(CO)_{12}$	37	trace
6	$RuCl_2(PPh_3)_3$	0	9 [d]
7	$Pd(OAc)_2$	47 [e]	0
8	$Pd(OAc)_2$/P(o-Tol)$_3$	55	0

[a] A mixture of 5 mmol of bromostyrene, 10 mmol of methyl acrylate, 10 mmol of triethylamine and 0.1 mmol of catalyst was heated at 100°C for 4 h, or a mixture of 2.5 mmol of chlorostyrene, 5 mmol of methyl acrylate, 5 mmol of triethylamine and 0.25 mmol of catalyst was heated at 100°C for 22 h. [b] Isolated yields. [c] Na_2CO_3 was used in place of NEt_3. [d] GLC yield. [e] See ref. 8.

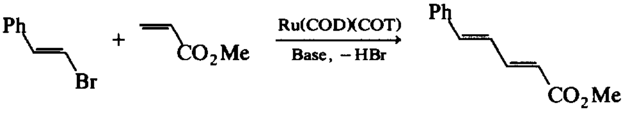
When the diene **3** was heated with methyl acrylate without the ruthenium catalyst, a mixture of the Diels–Alder adducts with the same distribution was obtained.

The reaction of β-chlorostyrene with methyl acrylate gave **3**, in 28% yield; 35% of the chlorostyrene charged was consumed in the presence of 2 mol% of Ru(COD)(COT) (Run 8). In the presence of 10 mol% of the catalyst, β-chlorostyrene was converted completely. The high conversion of chlorostyrene did not result in a high yield of the diene **3** because chlorostyrene was reduced to styrene as a by-product. Addition of P(p-PhF)$_3$ to Ru(COD)(COT) increased the yield of the 1,3-diene **3** (40%) (run 9). Addition of P(p-PhF)$_3$ inhibited the formation of styrene but at the same time depressed the conversion of chlorostyrene (run 9). The reaction of β-chlorostyrene with *N,N*-dimethylacrylamide gave the corresponding diene in 51% yield (run 11). Vinyl bromide, 1-bromopropene, 1-bromo-2,2-diphenylethylene and 1-bromo-2-methylpropene did not react with methyl acrylate under these reaction conditions. Olefins such as acrylonitrile or styrene did not react with β-bromostyrene.

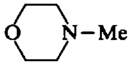
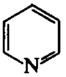
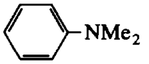
Catalytic activities of a series of ruthenium complexes in the reaction of β-bromostyrene with methyl acrylate were investigated and results are summarized in Table 2. $[RuCl_2C_6(CH_3)_6]_2$, $RuCl_3 \cdot nH_2O$ and $Ru_3(CO)_{12}$ as well as Ru(COD)(COT) showed catalytic activities and it should be noted that $RuCl_2(PPh_3)_3$, which is active in radical reactions [6,7], showed very low activity (Table 2, entry 6). Heck et al. reported that $Pd(OAc)_2$ catalyzes the reaction of β-bromostyrene with methyl acrylate to give the corresponding diene in 47% yield (Table 2, entry 7) [8]. When the reaction was performed in the presence of $Pd(OAc)_2$-P(o-Tol)$_3$, which is known to be an active catalyst for dehydrohalogenative coupling [9], the same product was obtained in 55% yield (Table 2, entry 8). In the reaction of chlorostyrene, palladium metal was deposited and the starting

Table 3

Reaction of β-bromostyrene with methyl acrylate—effects of various bases [a]



(1) (2) (3)

	Base	Mol. ratio 1/2	Yield of 3 (%)		Base	Mol. ratio 1/2	Yield of 3 (%)
1	NEt_3	1/2	68	5	NaOAc	1/5	13
2		1/2	55	6		1/1.2	0
3	N^nBu_3	1/1.2	48	7		1/1.2	trace
4	Proton sponge [b]	1/5	46				

[a] A mixture of β-bromostyrene (5 mmol), methyl acrylate (25 mmol), 2 mol% of catalyst and the base at 100°C for 4 h. [b] *N,N,N′,N′*-Tetramethyl-1,8-naphthalenediamine.

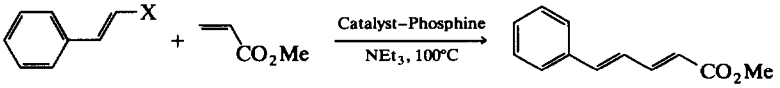
materials were recovered completely (Table 2, entries 7 and 8). Thus the reaction of chlorostyrene is characteristic of the ruthenium complex catalyst.

Effects of various bases were shown in Table 3. Triethylamine was the most effective. In contrast when NaOAc, pyridine and dimethylphenylamine were used in place of NEt_3 yields were very low.

Effects of addition of various phosphines on the reaction of β-bromostyrene (catalyst; $RuCl_3 \cdot nH_2O$) and on the reaction of β-chlorostyrene (catalyst; Ru(COD)(COT)) with methyl acrylate are summarized in Table 4. In the reaction of β-bromostyrene, $P(o\text{-Tol})_3$ did not disturb the reaction but addition of the other aromatic and aliphatic tertiary phosphines decreased catalytic activity. It is supposed that some stable ruthenium complex with added phosphines would be formed. In the case of $P(o\text{-Tol})_3$ such a stable complex would not be formed because of its bulkiness. In the reaction of β-chlorostyrene, addition of a series of

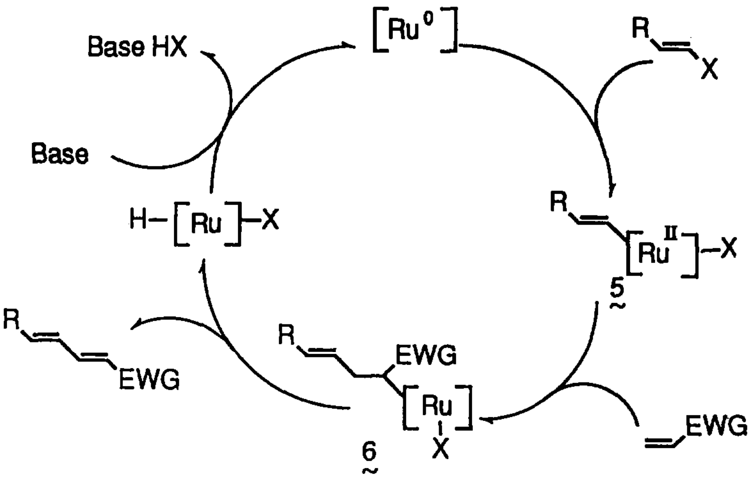
Table 4

Effects of phosphines on the reaction of β-halostyrene with methyl acrylate [a]



	Phosphine	Yield (%) [b] X = Br	Yield (%) [b] X = Cl	No.	Phosphine	Yield (%) [b] X = Br	Yield (%) [b] X = Cl
1	–	68	28	5	P^nBu_3	14	trace
2	$P(p\text{-PhF})_3$	34	40	6	PCy_3	27	12
3	$P(o\text{-Tol})_3$	66	28	7	$P(OPh)_3$	0	4
4	PPh_3	10	6	8	DPPE [c]	0	trace

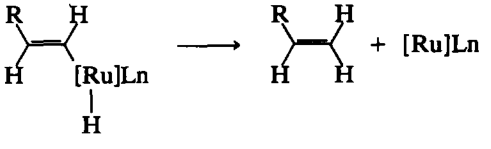
[a] Reactions of β-bromostyrene (5 mmol) with methyl acrylate (10 mmol) were catalyzed by $RuCl_3 \cdot nH_2O$ (2 mol%) and those of β-chlorostyrene by Ru(COD)(COT) (10 mol%). [b] Yields were based on the amount of halostyrenes. [c] Diphenylphosphinoethane.



Scheme 1.

phosphines, especially alkyl phosphines, again reduced the yields of the products, while without phosphines the coupling product was obtained in moderate yields. Exceptionally, $P(p\text{-}PhF)_3$ improved the yield to 40% (Table 4, entry 2).

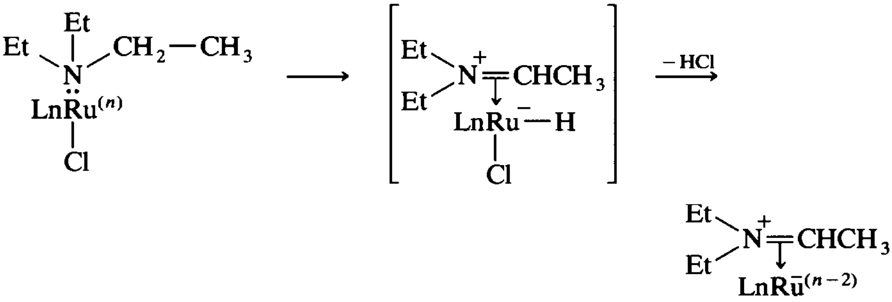
This reaction would proceed via a mechanism which is similar to that proposed for the palladium catalyst [8] (Scheme 1). Considering the fact that zero valent Ru(COD)(COT) is the best catalyst and $[RuCl_2C_6(CH_3)_6]_2$-EtOH-Na_2CO_3 is also a good catalyst but $RuCl_2(PPh_3)_3$ is not effective, the oxidative addition of a vinyl halide to a zero valent ruthenium complex would give an alkenyl Ru^{II} complex **5**, followed by insertion of an olefin to give a homoallyl ruthenium complex **6**. Then the β-elimination would generate the corresponding diene. Reductive elimination of the hydrogen halide enhanced by the base such as triethylamine would complete the $Ru^0 \rightleftharpoons Ru^{II}$ catalytic cycle. A certain hydride transfer prior to the insertion of the olefin into the alkenyl–Ru bond in the complex **5** to give a hydrido(alkenyl)ruthenium complex **7** and successive reductive elimination would give the by-product, olefin **8**.



(4)

(7) (8)

Indeed, when the reaction of Ru(COD)(COT) with an equimolar amount of bromostyrene in C_6D_6 was monitored by ^1H NMR, the formation of styrene (yield 60%) was confirmed at 60°C after 0.5 h. This fact supports that oxidative addition of an alkenyl halide should occur in the first step of this catalytic cycle. It is confusing that $RuCl_3 \cdot nH_2O$ is also an effective catalyst. It would be tentatively explained by a certain pathway to reduce $Ru^{III}Cl_3 \cdot nH_2O$ to Ru^0 in the presence of tertiary amine such as triethylamine. Without triethylamine, the reaction did not proceed. In the reaction of methyl acrylate (10 mmol) with triethylamine (10 mmol) in the presence of $RuCl_3 \cdot nH_2O$ (1.0 mmol, $n = 3$) at 100°C, formation of an adduct of diethylamine with methyl acrylate, methyl 3-(*N*,*N*-diethyl-amino)propionate (0.93 mmol, 93% based on the amount of Ru) and a trace amount (less than 1%) of diethylamine was confirmed. One possible mechanism is that the abstraction of β-hydrogen of a coordinated triethylamine and the reductive elimination of hydrogen chloride would give a lower valent ruthenium diethyliminium complex (eq. 5) which gives diethylamine by hydrolysis. Attempts to isolate such intermediate complexes were unsuccessful because of their high lability.



(5)

Even though the scope of the reaction is limited, it was discovered that some ruthenium complexes are active for dehydrohalogenative coupling of vinyl halides with olefins with electron-withdrawing groups. In some cases, ruthenium complexes are more effective catalysts than palladium complexes; even the sp^2-carbon-chlorine bond of β-chlorostyrene was activated by ruthenium complexes.

Experimental

IR spectra were measured on a Nicolet 5MX FT-IR spectrometer, the ^{1}H NMR and the ^{13}C NMR spectra with a JEOL GSX-270 spectrometer. Samples were dissolved in $CDCl_3$, and chemical shifts expressed relative to TMS as internal standard. Mass spectra were taken on a Shimadzu GCMS-QP2000 GC-mass spectrometer. Gas chromatographic analysis (GLC) were performed on a Shimadzu GC-8A with a FID detector. In some cases, yields were determined by the internal standard method according to the calibration curve obtained for each product in separate experiments. Microanalyses were performed by the Laboratory for Organic Elemental Microanalysis of Kyoto University. Methyl acrylate, methyl methacrylate and methyl vinyl ketone were commercial materials. $RuCl_3 \cdot nH_2O$ (Engelhard Chemicals), $Ru_3(CO)_{12}$ (Strem Chemicals) and $Pd(OAc)_2$ (Nakarai Chemicals) were used as received. (*E*)- and (*Z*)-β-bromostyrene [10] and β-chlorostyrene ($E/Z = 1/2$) [11] were prepared by methods described in the literature, as were Ru(COD)(COT) [12], $RuCl_2(PPh_3)_3$ [13] and $RuH_2(CO)[P(p\text{-}PhF)_3]_3$ [14].

General reaction procedure

The reaction of β-bromostyrene with methyl acrylate is representative. A mixture of β-bromostyrene (0.64 ml, 5 mmol), methyl acrylate (0.90 ml, 10 mmol), NEt_3 (1.4 ml, 10 mmol), and Ru(COD)(COT) (0.032 g, 0.1 mmol) was heated in a heavy walled sealed tube under argon at 100°C for 4 h, producing a mixture containing colourless needles to which was added 10 ml of water. This was extracted with three 10 ml portions of diethyl ether. The organic layer was dried over anhydrous $MgSO_4$. After evaporation of the ether, Kugelrohr distillation of the residue under reduced pressure afforded 1.64 g (yield 68%) of methyl (*E*,*E*)-5-phenyl-2,4-pentadienoate as white crystals.

All products obtained are known compounds and were identified by comparing their spectroscopic data with those in the literatures. Some ^{1}H NMR (270 MHz) and ^{13}C NMR (67.8 MHz) spectral data are shown below.

Methyl(2E,4E)-5-phenyl-2,4-pentadienoate. M.p. 69–71°C (Lit. [15] 71°C). IR (KBr): 1721, 1630 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ ppm): 3.76 (s, 3H, OCH_3), 5.99 (d, $J = 15.4$ Hz, 1H), 6.85–6.88 (m, 2H), 7.29–7.50 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, δ ppm): 51.5 (q), 120.8 (d), 126.2 (d), 127.7 (d), 128.8 (d), 129.1 (d), 136.0 (s), 140.5 (d), 144.8 (d), 167.4 (s).

The reaction of (*Z*)-β-bromostyrene with methyl acrylate gave a mixture of **3** and methyl (2*E*,4*Z*)-5-phenyl-2,4-pentadienoate **9** (**3**/**9** = 66/34). The product **7** could not be purified and it was obtained as a mixture with **3**.

Methyl(2E,4Z)-5-phenyl-2,4-pentadienoate [7]. ^{1}H NMR ($CDCl_3$, δ ppm): 3.74 (s), 6.04 (d, $J = 15.4$ Hz), 6.36 (dd, $J = 11.7$, 11.4 Hz), 6.82 (d, $J = 11.4$ Hz), 7.79 (dd, $J = 15.4$, 11.7 Hz).

Methyl 2-methyl-5-phenyl-2,4-pentadienoate [16]. ^{1}H NMR ($CDCl_3$, δ ppm): 2.05 (s, 3H, CH_3), 3.77 (s, 3H, OCH_3), 6.82–7.10 (m, 3H, olefin), 7.20–7.48 (m, 5H, Ph).

(E,E)-N,N-Dimethyl-5-phenyl-2,4-pentadienamide [17]. ^{1}H NMR ($CDCl_3$, δ ppm): 3.04 (s, 3H), 3.12 (s, 3H), 6.46 (d, 1H, $J = 15.0$ Hz), 6.90 (m, 2H), 7.23–7.49 (m, 5H + 1H).

(E,E)-6-Phenyl-3,5-hexadien-2-one. White needles. M.p. 66–67°C (Lit. [18] 68°C). IR (KBr): 1635, 1618 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ ppm): 2.31 (s, 3H, CH_3), 6.26 (d, 1H, $J = 15.3$ Hz), 6.88–6.99 (m, 2H), 7.24–7.48 (m, 5H + 1H). ^{13}C NMR ($CDCl_3$, δ ppm): 27.4 (q), 126.7 (d), 127.2 (d), 128.9 (d), 129.2 (d), 130.5 (d), 136.0 (s), 141.3 (d), 143.4 (d), 198.4 (s).

Dimethyl (E,E)-2-methyl-2,4-hexadienedioate [19]. ^{1}H NMR ($CDCl_3$, δ pm): 2.06 (d, 3H, $J = 1.8$ Hz), 3.78 (s, 3H), 3.79 (s, 3H), 6.16 (d, 1H, $J = 15.0$ Hz), 7.22 (dm, 1H, $J = 11.8$ Hz), 7.55 (dd, $J = 11.8$, 15.0 Hz).

The reaction of triethylamine with methyl acrylate catalyzed by $RuCl_3 \cdot nH_2O$ was performed as follows. A mixture of triethylamine (1.0 g, 10 mmol), methyl acrylate (0.86 g, 10 mmol), $RuCl_3 \cdot nH_2O$ (0.27 g, 1.0 mmol, $n \simeq 3$) was heated in an ampoule under an atmosphere of argon at 100°C for 10 h. The product was separated by Kugelrohr distillation and it was identified as methyl 3-(*N*,*N*-diethylamino)propionate by comparing its NMR, IR and mass spectra with those of the authentic sample. The amount of the product was determined by means of GLC (OV-17, 2.9 m, 3 mm-I.D.) using n-nonane as an internal standard. The needle crystals formed were dissolved in 1 ml of water. The solution was treated with 5% aq. NaOH and extracted with 2 ml of toluene. In the extract, a trace amount of (less than 0.01 mmol) of diethyl amine was detected by GC-mass.

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