Review

Novel organic syntheses catalyzed by (cyclooctadiene)(cyclooctatriene)ruthenium and its derivatives

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(Received December 28th, 1986)

Abstract

The characteristic catalytic activities of low valence ruthenium complexes, (cyclooctadiene)(cyclooctatriene)ruthenium and its derivatives, in organic syntheses have been exhibited by reviewing the recently developed novel reactions; (1) the first linear co-dimerization of acetylenes with 1,3-dienes (2) the [2 + 2] cross cycloaddition of norbornenes with dimethyl acetylenedicarboxylate (3) the addition of carboxylic acid to acetylenes giving enol esters.

When the chemistries of the three metals of the second row in the Group VIII (palladium, rhodium and ruthenium) were compared from the viewpoint of catalytic organic syntheses, the chemistry of ruthenium was found to be far behind the others [1]. One of the reasons for this is that the chemistry of palladium and rhodium has been developed with industrial processes such as the Wacker process, and the hydrogenation and hydroformylation of olefins, respectively, while ruthenium has found no such application. Another reason is that an appropriate zero-valent mononuclear ruthenium complex which gives a 16-electron species in solution is not readily available; attempts to synthesize zero-valent triphenylphosphine complexes were often unsuccessful because of the ortho metallation reaction to form a Ru^{II} complex [e.g. 2], which is usually inactive for catalytic reactions.

Recently, however, the organic syntheses catalyzed by ruthenium complexes have shown much development, and includes the activation of alcohols [3] and amines [4] catalyzed by $RuCl_2(PPh_3)_3$ or $RuH_2(PPh_3)_4$, selective hydrogenation of olefins [5], carbonyl groups [6] or aromatic rings [7], asymmetric hydrogenation of olefins [8], asymmetric hydrogen transfer reactions [9], hydrogenation of carbon monoxide [10], addition of polyhaloalkanes to olefins [11], preparation of dienes by desulfonylation [12], oxidation of olefins [13], isomerization of 1,4-epiperoxide [14] and a series of novel organic syntheses catalyzed by Ru(COD)(COT) (COD = cyclooctadiene, COT = cyclooctatriene) and its derivatives [15–17]. Ru(COD)(COT) is a zero-valent
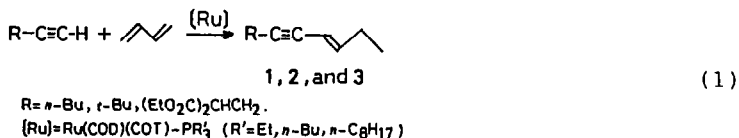
complex which can be readily prepared in high yield [18], and it is possible to leave it in air for more than 10 minutes without loss of activity. Recently it has been found that the derivatives of Ru(COD)(COT) such as bis(η^5-cyclooctadienyl)ruthenium also show remarkably high catalytic activity in organic syntheses which are catalyzed by ruthenium [17]. This is a brief review of the organic syntheses which are catalyzed by Ru(COD)(COT) and its derivatives.

Preparation of Ru(COD)(COT) and its derivatives

The complex Ru(COD)(COT) was firstly prepared in low yield by E.O. Fischer in 1963 [19]. Recently the method of preparation was improved by Pertici [18a,b] and Itoh [18c]; now the complex can be obtained pure in > 80% yield. This complex can be stored under argon for several months. Ru(COD)(COT) is the parent complex of various low- and high-valence ruthenium complexes which show catalytic activity in organic syntheses. Selected examples are shown in Scheme 1.
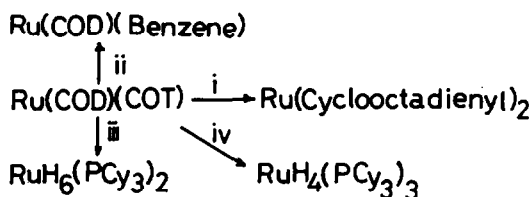
Linear co-dimerization of terminal acetylenes with 1,3-dienes

Recently it was found that a Ru(COD)(COT)/PR$_3$ system catalyzes a reaction with novel carbon–carbon bond formation; selective linear co-dimerization of a terminal acetylene with 1,3-butadiene (eq. 1) [15b].

$$R-C\equiv C-H + /\!\!\!\!\diagup\!\!\!\!\diagup \xrightarrow{\text{(Ru)}} R-C\equiv C-\diagdown\diagup\diagdown$$

$$1,2,\text{and }3$$

$$(1)$$

R= n-Bu, t-Bu, (EtO$_2$C)$_2$CHCH$_2$.
(Ru)=Ru(COD)(COT)-PR$_3'$ (R'=Et, n-Bu, n-C$_8$H$_{17}$)

This reaction is the first example of the linear co-dimerization of terminal acetylenes and 1,3-dienes. The reaction is also well catalyzed by RuH$_2$(PR$_3$)$_4$ (R' = alkyl) [15a]. Because the catalytic profiles of both complexes are similar, the reactions proceed via a common active species. Ru(COD)(COT) is more convenient to use, since its preparation is much simpler than that of RuH$_2$(PR$_3$)$_4$. Results are summarized in Table 1. Most reactions proceed at 60–100 ° C and are chemo-, regio- and stereoselective.

1-Hexyne or 3,3-dimethyl-1-butyne readily reacts with 1,3-butadiene in the presence of a catalytic amount of Ru(COD)(COT)/PBu$_3$ or RuH$_2$(PBu$_3$)$_4$ in benzene at 60–80 ° C for 4 h to give (*E*)-3-decen-5-yne (1) or (*E*)-7,7-dimethyl-3-octen-5-yne (2) in excellent yields with high regio- and stereoselectivity (runs 1, 2, 4). Neither the branched isomer nor the cyclic oligomers were formed. The stereochemistry of the olefinic group is completely *trans*.

Ru(COD)(Benzene)
↑ ii
Ru(COD)(COT) —i→ Ru(Cyclooctadienyl)$_2$
↓ iii   ↘ iv
RuH$_6$(PCy$_3$)$_2$ RuH$_4$(PCy$_3$)$_3$

Scheme 1. i. Toluene reflux, ref. 18a. ii. H$_2$, benzene, r.t. ref. 20. iii. H$_2$, 2PCy$_3$, r.t. ref. 21. iv. H$_2$, 3PCy$_3$, ref. 21.

Table 1

Linear codimerization of acetylenes and 1,3-dienes catalysed by Ru(COD)(COT)/PBu$_3$ and RuH$_2$(PBu$_3$)$_4$ [a]

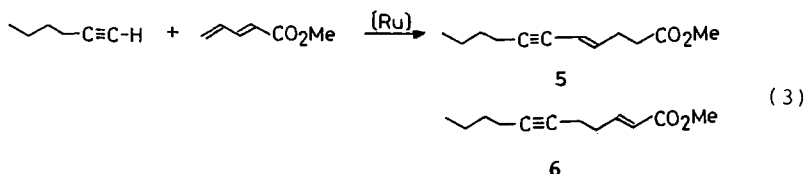| Run	Acetylene	Diene (mmol)	Catalyst [b]	mmol	Temp. °C	Time (h)	Product	Yield %
1	1-Hexyne	1,3-Butadiene (20)	A/PBu$_3$	0.1/0.2	80	4	(structure, C≡C)	94
2	3,3-Dimethyl-1-butyne	1,3-Butadiene (20)	A/PBu$_3$	0.1/0.2	80	4	(structure, C≡C)	96
3	1-Pentyne	1,3-Butadiene (20)	B	0.1	60	2	(structure, C≡C)	96
4	3,3-Dimethyl-1-butyne	1,3-Butadiene (20)	B	0.2	60	4	(structure, C≡C)	100
5	3,3-Dimethyl-1-butyne	Isoprene (10)	B	0.1	140	6	a (structure, C≡C) b (structure, C≡C)	a 55 a/b = 85/15 b
6	4,4-Dicarbo-ethoxy-1-butyne	1,3-Butadiene (20)	A/PBu$_3$	0.2/0.4	80	4	(EtO$_2$C)$_2$CHCH$_2$C≡C (structure)	80
7	1-Hexyne	Methyl (E)-2,4-pentadienoate (20)	A/PBu$_3$	0.1/0.2	80	8	a (structure, C≡C—CO$_2$Me) b (structure, C≡C—CO$_2$Me)	32 a/b = 64/36 a b
8	1-Pentyne	Methyl (E)-2,4-pentadienoate (10)	B	0.1	60	10	a (structure, C≡C—CO$_2$Me) b (structure, C≡C—CO$_2$Me)	63 a/b = 60/40 a b
9	1-Hexyne	Methyl (E,E)-2,4-hexadienoate (15)	A/PBu$_3$	0.1/0.2	80	8	(structure, C≡C—CO$_2$Me)	45
10	4-Methyl-1-pentyne	Methyl (E,E)-2,4-hexadienoate	B	0.1	100	6	(structure, C≡C—CO$_2$Me)	68

[a] Solvent, benzene 5 ml; acetylene 10 mmol. [b] A = Ru(COD)(COT), ref. 15b; B = RuH$_2$(PBu$_3$)$_4$, ref. 15a.

On the other hand, the reaction of 1-hexyne with methyl (E,E)-2,4-hexadienoate gave methyl (E)-5-methyl-2-undecen-6-ynoate (4) in 45% yield (eq. 2).
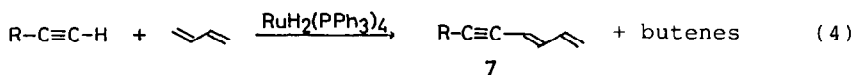
$$\text{\textbackslash/\textbackslash—C≡C-H} \quad + \quad \text{\textbackslash/\textbackslash/\textbackslash/CO}_2\text{Me} \quad \xrightarrow{\text{[Ru]}} \quad \text{\textbackslash/\textbackslash—C≡C—\textbackslash/\textbackslash/CO}_2\text{Me} \qquad (2)$$
$$\mathbf{4}$$
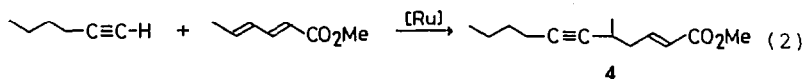
The reaction of 1-hexyne with methyl (E)-2,4-pentadienoate gave two isomers of the co-dimer, **5** and **6** (eq. 3).

$$\text{\textbackslash/\textbackslash—C≡C-H} \quad + \quad \text{/\textbackslash/\textbackslash/CO}_2\text{Me} \quad \xrightarrow{\text{[Ru]}} \quad \text{\textbackslash/\textbackslash—C≡C—\textbackslash/\textbackslash/CO}_2\text{Me}$$
$$\mathbf{5}$$
$$\text{\textbackslash/\textbackslash—C≡C—\textbackslash/\textbackslash/CO}_2\text{Me} \qquad (3)$$
$$\mathbf{6}$$

The optimum ratio of PBu_3/Ru was 2.0. In the absence of PBu_3 under the reaction conditions shown in run 1, the yield of the co-dimer was 1%. Trialkylphosphines with cone angles of ca. $130°C$ such as triethylphosphine, tributylphosphine and trioctylphosphine were effective as ligands, however, trimethylphosphine, triisopropylphosphine, tricyclohexylphosphine, arylphosphines or phosphites were not. The polarity of the solvents (benzene, toluene, THF, acetonitrile, dichloromethane and DMF) only slightly affected the yields of co-dimer.
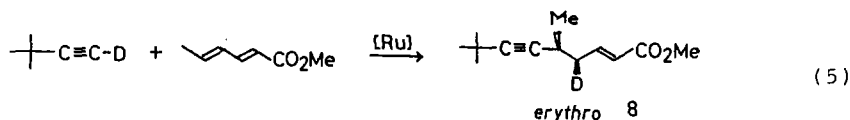
On the other hand, when $RuH_2(PPh_3)_4$ was used in the system, oxidative co-coupling of the acetylene and 1,3-diene occurred to give the dieneyne **7** (eq. 4) [15a].

$$\text{R-C≡C-H} \quad + \quad \text{\textbackslash/\textbackslash} \quad \xrightarrow{\text{RuH}_2\text{(PPh}_3)_4} \quad \text{R-C≡C—\textbackslash/\textbackslash} \quad + \text{ butenes} \qquad (4)$$
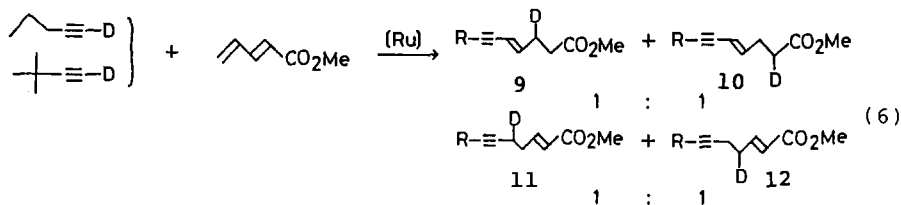$$\mathbf{7}$$

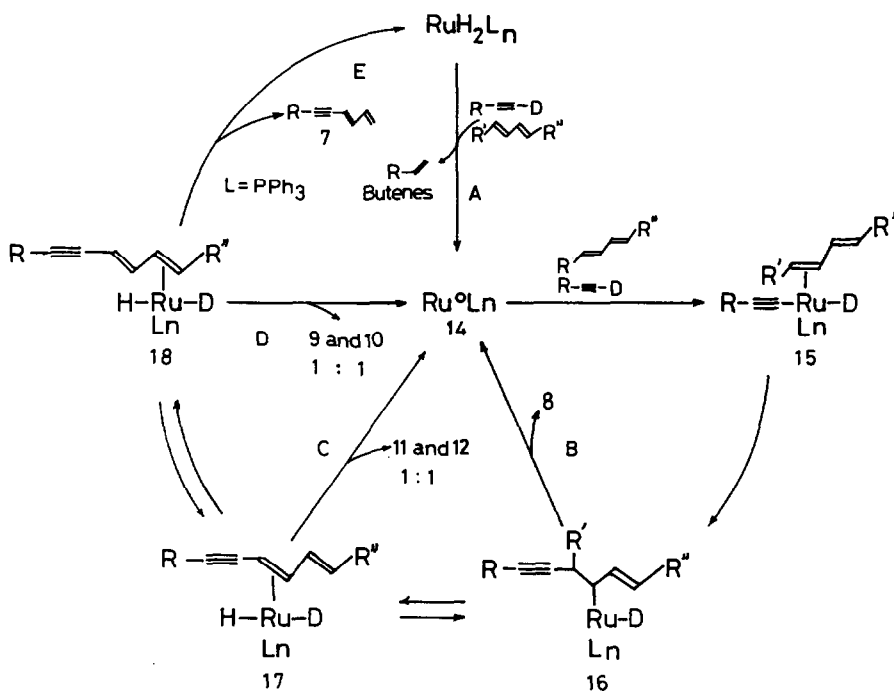$R = n\text{-Pr}, n\text{-Bu}, n\text{-C}_6\text{H}_{13}.$

In this case deactivation of the catalyst was observed, probably owing to the ortho-metallation of the active zero-valent complex to form Ru^{II} complexes.

The reaction of 3,3-dimethyl-1-butyne-1-d with methyl (E,E)-2,4-hexadienoate gave *erythro* methyl (E)-5,8,8-trimethyl-2-nonen-6-ynoate-4-d (**8**) as the sole product (eq. 5). The deuterium was introduced selectively at the 4 position of the co-dimer via a *cis* addition pathway.
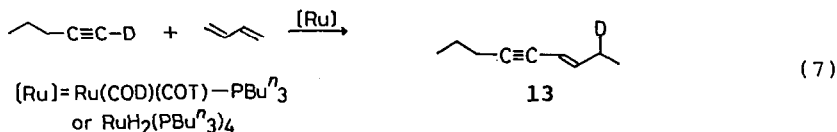
$$\text{+C≡C-D} \quad + \quad \text{\textbackslash/\textbackslash/\textbackslash/CO}_2\text{Me} \quad \xrightarrow{\text{[Ru]}} \quad \overset{\text{Me}}{\text{+C≡C—\underset{D}{\textbackslash}/\textbackslash/CO}_2\text{Me}} \qquad (5)$$
$$\textit{erythro} \quad \mathbf{8}$$

The reaction of 1-pentyne-1-d with methyl (E)-2,4-pentadienoate gave four isomers of the co-dimer, **9–12**. The ratio $(9+10)/(11+12)$ was 6/4, with the ratios **9/10** and **11/12** being both 1/1 (eq. 6).

$$\left. \begin{array}{l} \text{/\textbackslash—≡—D} \\ \text{+—≡—D} \end{array} \right\} \quad + \quad \text{/\textbackslash/\textbackslash/CO}_2\text{Me} \quad \xrightarrow{\text{[Ru]}} \quad \underset{\mathbf{9}}{\text{R-≡—\textbackslash/\underset{D}{\textbackslash}/CO}_2\text{Me}} \quad + \quad \underset{\mathbf{10}}{\text{R-≡—\textbackslash/\underset{D}{\vee}/CO}_2\text{Me}}$$
$$1 \quad : \quad 1$$
$$\underset{\mathbf{11}}{\text{R-≡—\overset{D}{\underset{}{\textbackslash}}/\textbackslash/CO}_2\text{Me}} \quad + \quad \underset{\mathbf{12}}{\text{R-≡—\textbackslash/\underset{D}{\vee}/CO}_2\text{Me}} \qquad (6)$$
$$1 \quad : \quad 1$$

RuH$_2$L$_n$

E

L = PPh$_3$

7

R Butenes

A

R—≡—D
R'⌒⌒⌒R"

R—≡——R"
H–Ru–D
Ln
18

D   9 and 10
     1 : 1

Ru°Ln
14

R—≡–D

R'—⌒R"

R'⌒R"
R–≡–Ru–D
Ln
15

C   11 and 12
     1 : 1

8

B

R—≡—⌒⌒R"
H—Ru–D
Ln
17

R—≡—⌒R"
Ru–D
Ln
16

Scheme 2. Proposed mechanism of the co-dimerization of acetylenes with 1,3-dienes.

The reaction of 3,3-dimethyl-1-butyne-1-d with methyl (E)-2,4-pentadienoate gave a result similar to that described above. It should be noted that no deuterium was introduced into the olefinic group of the products. The reaction of 1-pentyne-1-d with 1,3-butadiene gave, to our surprise, (E)-3-nonene-5-yne-2-d (13) as the sole product. Deuterium was introduced selectively at the 2 position of the co-dimer (eq. 7).

$$\text{⌒—C≡C–D} \ + \ \text{⌒} \xrightarrow{\text{[Ru]}} \text{⌒—C≡C–⌒} \qquad (7)$$

[Ru] = Ru(COD)(COT)—PBu$^n_3$
or RuH$_2$(PBu$^n_3$)$_4$

13

There is no clear-cut mechanism which accounts for these complicated results. Obviously, the mechanism of the formation of 8 is different from that of 13 because the position at which the deuterium is introduced is different. The path of the formation of the linear codimers 8 and 9–12 is shown in Scheme 2. Taking into account that both Ru(COD)(COT)/PBu$_3$ and RuH$_2$(PBu$_3$)$_4$ show almost the same catalytic activities and identical distributions of the deuterium introduced into the reaction of acetylene-d (eqs. 5, 6 and 7), the reaction mechanism should be the same for both catalysts. The first step of the catalytic cycle would be the oxidative addition of acetylene to a zero-valent ruthenium complex 14 such as Ru(PR$_3$)$_n$ derived from the reaction of Ru(COD)(COT) with trialkylphosphines or by the reaction of RuH$_2$(PBu$_3$)$_4$ with the diene or acetylenes. It has been reported that the reaction of RuH$_2$(PPh$_3$)$_4$ with olefins such as ethylene or styrene gives a zerovalent

ruthenium complex Ru(olefin)(PPh$_3$)$_4$ in the early stages of the reaction [2,22]. The formation of a zero-valent ruthenium complex was also reasonably assumed in [2 + 2] cross addition of norbornenes with acetylene catalyzed by RuH$_2$(PPh$_3$)$_4$ [16a], where η^2-coordination of the diene to the complex gives **15**. On the other hand, insertion of the diene into the Ru-alkyl bond would give **16**. If acetylene, instead of the diene, coordinates and inserts into the Ru-alkynyl bond, homo-oligomerization of acetylene proceeds. To prevent the insertion of acetylene, a molar ratio 2 of 1,3-diene/acetylene was required for butadiene. When R' and R'' in **16** are Me and CO$_2$Me, respectively, i.e. in the reaction of methyl (E,E)-2,4-hexadienoate, the reductive elimination of the ligands would give **8** selectively. Considering the high chemo- and regioselectivity of the reaction and the fact that the deuterium is not introduced into the olefinic group of **9–12**, the formation of an intermediate, **19**, with a branched skeleton or, **20**, derived by the insertion of the diene into the Ru–D bond is ruled out. Complex **19** will not give a linear co-dimer. If **20** is formed, the formation of **9–12** without deuterium at the olefinic group and the distributions of the deuterium cannot be explained.

19   20
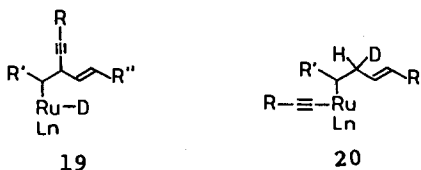
The possibility of the isomerization of **6** to **5** was investigated. The reaction of 1-hexyne with methyl (E,E)-2,4-hexadienoate was carried out in the presence of **6**; product **4** was obtained and **6** was recovered without the formation of **5** (eq. 8).
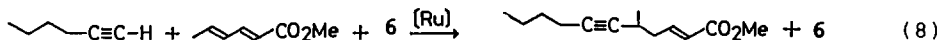
This, and the fact that deuterium is not introduced into the olefinic group in **9–12** strongly suggest that when R' is hydrogen, i.e. in the reaction of methyl (E)-2,4-pentadienoate, β-elimination of **16** readily occurs giving the equilibrium mixture deuteridohydrido(η^2-dienyne)ruthenium complex **17** and its isomer **18**. The hydrogenation of the coordinated dienyne in **17** or **18** gives two pairs of olefins (**11** and **12**), and (**9** and **10**), in both pairs the equivalent amount of deuterium is introduced into the methylene group and no deuterium is introduced into the olefinic groups. In these steps the zerovalent ruthenium complex **14** is reenerated (paths C and D). It is unlikely that π-allyl complexes such as **21** play the role of key intermediate because the formation of **9–12** cannot be explained. When the ligand L in complexes **17** and **18** is triphenylphosphine, the dissociation of the dienyne occurred readily to give **7** (Path E, eq. 4). The main reason for the dissociation of **7** is due to the larger cone angle of triphenylphosphine (145°) compared with that of tri-butylphosphine (130°). The reaction path of the co-dimerization of 1-pentyne-1-d with 1,3-butadiene is confused. A tentative mechanism including a π-allyl(alkynyl) deuteridoruthenium complex is proposed.
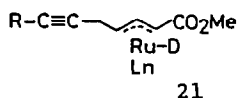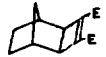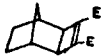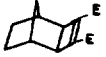

21
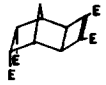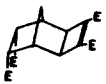
Table 2

[2 + 2] cross cycloaddition of norbornenes with dimethyl acetylenedicarboxylate [a]

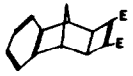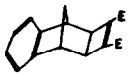| Run	Norbornenes	Catalyst (mmol)	Temp. °C	Time (h)	Product	Yield % [b]
1 [d]	Norbornene	RuH$_2$(PPh$_3$)$_4$ (0.2)	80	24		65(52)
2 [c]	Norbornene	Ru(COD)(COT) (0.1) PBu$_3$ (0.2)	100	6		99
3 [d]	Norbornene	RuH$_2$(CO)[P(p-PhF)$_3$]$_3$ (0.24)	100	6		
4 [d]		RuH$_2$(PPh$_3$)$_4$ (0.2)	100	6		64(48)
5 [d]		RuH$_2$(CO)[P(p-PhF)$_3$]$_3$ (0.24)	100	6		88
6		Ru(COD)(COT) (0.4)	100	6		52(40)
7		Ru(COD)(COT) (0.4)	100	6		(67)

[a] Solvent, benzene 10 ml. Norbornenes, 10 mmol. Dimethyl acetylenedicarboxylate 10 mmol. E = COOMe. [b] GC yield. Isolated yields are given in the parentheses. [c] Dimethyl acetylenedicarboxylate, 15 mmol. [d] Ref. 16a, others 16b.
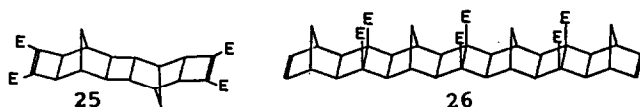
[2 + 2] Cross cycloaddition of norbornenes with dimethyl acetylenedicarboxylate

Ru(COD)(COT) catalyzes the [2 + 2] cross addition of norbornenes with dimethyl acetylenedicarboxylate (eq. 9) [16].

(9)
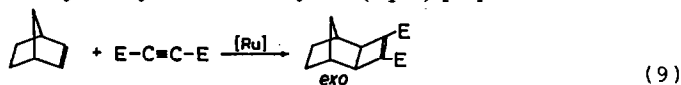
[Ru] = Ru(COD)(COT)-PR$_3$ or RuH$_2$(CO)(PR$_3$)$_3$ E = CO$_2$Me

This reaction is also well catalyzed by RuH$_2$(CO)[P(p-FC$_6$H$_4$)$_3$]$_3$ [16a]. The results of these are shown in Table 2. The cross cyclo-addition of norbornadiene with acetylenes catalyzed by Ni complexes is well known; however, norbornene showed no reaction. The ability to activate norbornene is unique to ruthenium. The reaction is a selective *exo*-addition and the catalytic cycle Ru^0 $\rightleftharpoons$ Ru^{II} via a ruthenacyclo-pentene complex 24 is proposed (Scheme 3). Using this reaction linear polycyclic compounds such as 25 [16a] and 26 [23] (ladder oligomers) were synthesized.

25

26
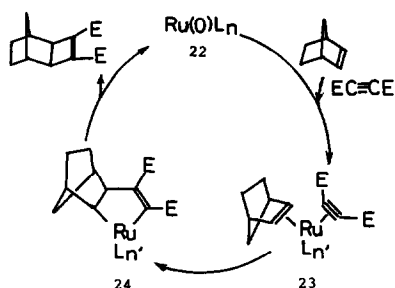
Scheme 3. Proposed mechanism of the [2+2] cross cycloaddition of norbornene with dimethyl acetylenedicarboxylate.

Addition of carboxylic acids to acetylenes catalyzed by $Ru(cyclooctadienyl)_2/PR_3$
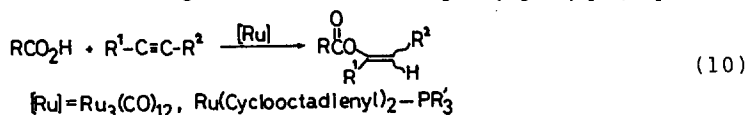
Quite recently, the addition of carboxylic acids to acetylenes catalyzed by ruthenium complexes has been developed (eq. 10) [17,24].

$$RCO_2H + R^1-C≡C-R^2 \xrightarrow{[Ru]} \quad (10)$$

$$[Ru] = Ru_3(CO)_{12}, \quad Ru(Cyclooctadienyl)_2-PR_3$$

Shvo reported that $Ru_3(CO)_{12}$ catalyzes the addition of carboxylic acids to mainly internal acetylenes at 145°C to give enol esters [24]. On the other hand it has been found that $Ru(cyclooctadienyl)_2/PR_3$/maleic anhydride catalyzes the addition of carboxylic acid to terminal acetylene [17]. The regioselectivity can be controlled by selecting an appropriate phosphine or solvent. Typical results of these reactions are shown in Table 3. It is well known that Hg salts catalyze the addition of carboxylic acid to acetylene [25]. However, because of the toxicity of the catalyst and the limited compatibility with the functional groups, improvement of the catalysts was required. Kinetic analysis of the reaction using $Ru(cyclooctadienyl)_2$ as the catalyst showed that the rate was represented by the following equation,

$$rate = k[Ru]_0[acetylene][RCO_2H]$$

where $[Ru]_0$ is the initial concentration of the ruthenium catalyst [26]. Taking into account the distribution of the deuterium in the reaction of acetic acid-d, which showed *trans*-addition, nucleophilic attack by the carboxylate ion on the coordinated acetylene was postulated to be the rate determining step [26]. These reactions can be applied to acids having various kinds of functional groups. In the reaction of propargyl carbonate with acetic acid, the regioselectivity of the product was 100% and the product, **27**, was an allyl carbonate. The carbonate **27** reacts with carbonucleophiles such as **28** in the presence of a palladium catalyst to give polyfunctional enol ester **29** which is difficult to synthesize by other methods [17c]. These reactions suggest that the combination of the chemistry of the ruthenium and palladium would open up a whole new field in organic synthesis.
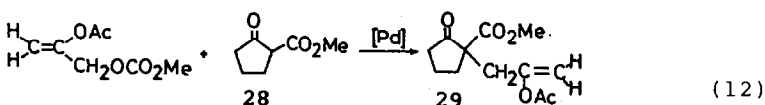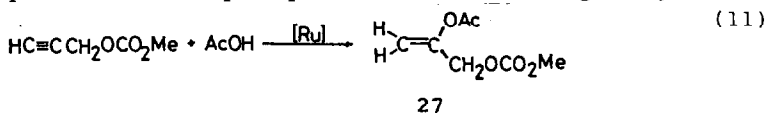

$$HC≡C CH_2OCO_2Me + AcOH \xrightarrow{[Ru]} \quad (11)$$

27

$$(12)$$

28 **29**

Table 3

Ruthenium catalyzed addition of carboxylic acids to acetylenes [a]

Run	R (of RCOOH =) mmol	Acetylene (mmol)	Catalyst (mmol)	Temp. (°C)	Time (h)	Products (%) $RCO_2C=CH_2$ $|$ R'	$RCO_2CR=CHR'$ E and Z	Ref.
1	Ph [b]	$PhC \equiv CPh$	$Ru_3(CO)_{12}$	145	17	0	64 $E/Z = 18/82$	24
2	Ph	$PhC \equiv CH$	$Ru_3(CO)_{12}$	145	17	0	74 $E/Z = 81/19$	24
3	CH_3	$(n-C_3H_7)_2C_2$	$Ru_3(CO)_{12}$	145	17	0	92 $E = 100\%$	24
4	CH_3	$(MeO_2C)_2C_2$	$Ru_3(CO)_{12}$	145	17	0	95	24
5	CH_3 (10)	1-Hexyne (10)	A	80	4	99	1	17b
6	t-Bu (10)	1-Hexyne (10)	A	80	4	(69)	7	17b
7	1-Adamantyl	1-Hexyne (10)	A	80	4	91	2	17b
8	$n-C_{17}H_{35}$ (10)	1-Hexyne (10)	A	80	4	88	1	17b
9	$CH_2=CMe$ (10)	1-Pentyne (10)	B	80	4	93	4	17a
10	E-MeHC=CH (10)	3,3-Dimethyl-1-butyne (10)	B	80	4	(68)	–	17a
11	Ph (10)	1-Pentyne (10)	B	80	4	99(75)	–	17a
12	PhCO (10)	1-Hexyne (10)	A	80	4	88(59)	11	17b
13	PhCH(OH) (10)	1-Hexyne (10)	A	80	4	77	10	17b
14	$MeCOCH_2CH_2$ (10)	1-Hexyne (10)	A	80	4	60	4	17b
15	MeCONHCH(Me) (10)	1-Hexyne (10)	A	80	4	31	4	17b
16	$Et_2NH + CO_2$	1-Hexyne (10)	$Ru_3(CO)_{12}$	140	20	3	33 $E/Z = 45/55$	27
17	$Et_2NH + CO_2$	$PhC \equiv CH$	$Ru_3(CO)_{12}$	125	20		17 $E/Z = 65/35$	27
18	$Et_2NH + CO_2$	1-Hexyne	C	100	48		62 $E/Z = 8/92$	28
19	$\overline{C_5H_{10}NH} + CO_2$	1-Hexyne	C	100	72		52 $E/Z = 12/88$	28

[a] $Ru_3(CO)_{12}$ 4×10^{-3} M in toluene, [Acid] = [Acetylene] = 0.2 M. A, Ru(cyclooctadienyl)$_2$ 0.1 mmol, tributylphosphine 0.2 mmol; solvent, toluene 5 ml. B, Ru(cyclooctadienyl)$_2$ 0.1 mmol, tributylphosphine 0.2 mmol; solvent, benzene 5 ml. C, Ru(cyclooctadienyl)$_2$ 0.2 mmol, PCy$_3$ 0.4 mmol, maleic anhydride 0.2 mmol; solvent, Ru(cyclooctadienyl)$_2$ 0.2 mmol, maleic anhydride 0.4 mmol. [b] A considerable amount of rearranged products $Ph_2C=C(OCOR)H$ was formed.

One application of this reaction is the activation of carbon dioxide in the presence of a secondary amine and acetylene;

$$R_2NH + CO_2 + R'C\equiv CH \xrightarrow{[Ru]} \quad (13)$$
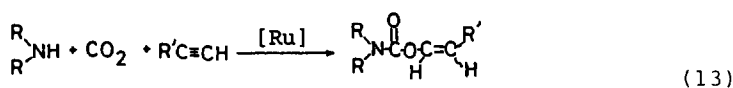
30

the products are vinyl carbamates (**30**) which are bioactive (eq. 13) [27]. Results are also summarized in Table 3. When $Ru_3(CO)_{12}$ was used as a catalyst, the yields and selectivity were rather low, however, when bis(cyclooctadienyl) ruthenium/PR_3/maleic anhydride is employed as catalyst, the reaction proceeded at a lower temperature and the selectivity for the enol ester was considerably improved [28].

Concluding remarks

These results show that the low valence ruthenium complexes, Ru(COD)(COT) and its derivatives, employed here have very high and characteristic activities which are different from those of other metals and other ruthenium complexes such as $Ru_3(CO)_{12}$, $RuCl_3$ or $RuCl_2(PPh_3)_3$. The co-dimerization of acetylenes with 1,3-dienes and the [2 + 2] cross cycloaddition are novel catalytic carbon-carbon bond formation reactions which are rationalized by $Ru^0 \rightleftharpoons Ru^{II}$ catalytic cycles. The greatest advantage of these catalytic systems is that one can "direct" the catalysts by selection of an appropriate ligand. Further studies on the catalytic activities of the systems Ru(COD)(COT)/PR_3 and Ru(η^5-cyclooctadienyl)$_2$/PR_3 are now in progress.

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