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C–H Bond activation of alkenecarboxylates by ruthenium complexes having triphenylphosphine ligands

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Abstract

Reactions of alkenecarboxylates with $RuH(C_2H_4)(PPh_3)_2(PPh_2C_6H_4)$ (**1**) or $RuH_2(PPh_3)_4$ (**2**) give hydrido(1-alkoxycarbonyl-η^3-allyl-C^1, C^3)ruthenium(II) complexes, $RuH(\eta^3\text{-}CH(R)CHCHCOOR')(PPh_3)_2$ (R = H, R' = Me (**3a**), Et (**3b**), *n*-Bu (**3c**), cyclohexyl (**3d**); R = Me, R' = Me (**4**); R = Et, R' = Me (**5a**), cyclohexyl (**5b**)) in benzene at room temperature. Reactions of **3a** with CO, iodine, methyl acrylate and ethyl methacrylate as well as the thermolysis result in the reductive elimination of methyl crotonate. In the presence of ethylene, complex **5b** is slowly converted into dienecarboxylate complexes with concomitant hydrogenation of ethylene to ethane.

1. Introduction

Carbon–hydrogen bond activation by transition metal complexes under mild conditions has attracted considerable interest in organometallic chemistry in recent years (see for example refs. 1). Although much attention has been focused on alkane activation in relation to the chemical utilization of LNG, specific C–H bond activation of functionalized organic molecules has also potential significance in the fields of catalysis and organic synthesis. We previously reported the formation of the hydrido(alkenyl)ruthenium(II) complex by the reaction of $RuH(C_2H_4)(PPh_3)_2(PPh_2C_6H_4)$ (**1**) with alkyl methacrylate with liberation of ethylene [2,3]. The same compound was also obtained by employing $RuH_2(PPh_3)_4$ (**2**) accompanied by concomitant liberation of alkyl isobutyrate under ambient conditions [4]. Both reactions are considered to involve oxidative addition of only β-vinylic C–H bond in the alkyl methacrylates to ruthenium(0), giving a hydrido(alkenyl)ruthenium(II) complex in which the ester group is actually coordinated to Ru. The reactions are highly regioselective and the importance of the prior formation of coordinatively unsaturated ruthenium(0) species has been suggested. A possible mechanism involving coordination of the carbonyl group of the ester to Ru to induce selective β-C–H activation has been ruled out, since the reaction of $RuHNp(dmpe)_2$ with methyl methacrylate only afforded a similar hydrido(alkenyl)ruthenium(II) complex having the ester group free from coordination [5]. Thus understanding of controlling factors of this unusual C–H bond activation reaction is still ambiguous and has been left unresolved. On the contrary, allylic C–H bond activation by transition metal complexes is frequently encountered in various organic reactions promoted by transition metals such as Pd and the evidence for the formation of π-allylpalladium species by deprotonation has been well established [6]. Direct oxidative addition of allylic C–H bond is also considered as an alternative process for the formation of π-allylmetal species. Such an oxidative addition process is unequivocally established by the facts found in a few transition metal systems such as Ni, Ir, Ru, Mo and W, including an equilibrium between a propylene complex and a hydrido(π-allyl) complex [7]. Formation of bis(π-allyl)ruthenium(II) complex on interaction of **2** with propylene is known. However, examples for such processes are still very limited so far. Thus the development of such direct allylic C–H bonds oxidative addition of olefins, especially when they contain various functional groups, is considerably significant from the point of applications to organic synthesis and funda-

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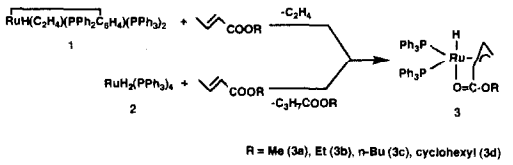
mentals of organometallic reactions, since most of the processes producing π-allyl metal complexes hitherto known are limited to oxidative addition of allyl halides, carboxylates and carbonates, addition of metal hydrides or protonation of diene complexes, and electrophilic and nucleophilic substitution of allyl compounds [8]. These led us to examine further reactivities of the ruthenium complexes **1** and **2** towards various substituted alkenecarboxylates. We wish to report the oxidative addition of sp^3 C–H bond in alkyl crotonates and related compounds to a ruthenium(0) complex having triphenylphosphine ligands, forming new π-allylruthenium complexes.

2. Results and discussion

2.1. Reactions of 1 and 2 with alkyl crotonates

The reaction of $RuH(C_2H_4)(PPh_3)_2(PPh_2C_6H_4)$ (**1**) or $RuH_2(PPh_3)_4$ (**2**) with alkyl crotonate $CH_3CH{=}CHCOOR$ (R = Me, Et, Bu, cyclohexyl (Cy)) in benzene gave yellow hydrido(1-alkoxycarbonyl-η^3-allyl-C^1, C^3)ruthenium complexes, $RuH(\eta^3\text{-}CH_2CHCHCOOR)(PPh_3)_2$ (R = Me (**3a**), Et (**3b**), ^{n}Bu (**3c**), Cy (**3d**)). These complexes were characterized mainly by nuclear magnetic resonance (NMR) and IR spectroscopy and elemental analysis as well as by chemical reactions. During the reactions, evolution of ethylene gas was observed in the case of **1** whereas, in the latter case, stoichiometric hydrogenation of alkyl crotonate was observed:



(1)

Similar reactions with alkyl 3-butenoate also afforded the same compounds. During the reaction, alkyl 3-butenoate used slowly isomerized to alkyl crotonate. Complexes **3** are possibly active intermediates in the isomerization, since **1** and **3** catalyze the isomerization at room temperature. However, it is not clear whether the isomerization took place prior to the C–H oxidative addition or not, since the observed rates of both isomerization of methyl 3-butenoate and formation of the π-allylruthenium complex **3a** in toluene-d_8 at 10°C were quite similar ($\tau_{1/2} \approx 40$ min in toluene-d_8 at 10°C). Independent catalytic cycles by hydride complexes formed in the reaction could be involved. At present we favour the mechanism involving oxidative addition of sp^3 C–H bonds in methyl crotonate and 3-butenoate to give π-allylruthenium complexes:

(2)

The reactions are considered to proceed via oxidative addition of alkyl crotonate or 3-butenoate to ruthenium(0) species which is produced either by consumption of the two hydrides in **2** by the hydrogenation of alkyl crotonate, or by the reverse orthometallation reaction in **1** followed by elimination of coordinated ethylene. Such processes producing zero-valent ruthenium species in the reactions of **2** with various unsaturated molecules have been well established previously [1,3,9].

Table 1 summarizes the ^{1}H NMR data for these complexes. ^{1}H NMR of **3a** shows a triplet at −24.3 ppm assignable to the hydride, indicating that **3a** contains two P ligands. Four magnetically non-equivalent protons for allylic moiety are observed at 5.82, 3.82, 2.84 and 2.45 ppm. Two terminal methylene protons show coupling with one of the P nuclei, suggesting that the methylene group is placed *trans* to one of the P ligands. Coupling between two terminal methylene protons was not observed, which was confirmed by ^{1}H–^{1}H COSY and homo decoupling techniques. Complexes **3b–3d** also show similar spectra to that of **3a**. In the ^{13}C NMR of **3a**, the terminal carbon appears as a double doublet at 56.3 ppm (J = 20.6, 3.2 Hz) and the

TABLE 1. ^{1}H NMR (C_6D_6, 200 MHz, room temperature) of π-allylruthenium(II) complexes RuH(RC(Ha)C(Hb)CR′COOR″)L_2

Complex	R	R′	R″	δ (with respect to tetramethylsilane) (ppm) (J (Hz))					
				Ha	R	Hb	R′	OR″	RuH
3a	H	H	Me	2.45, dd (12.2, 4.9)	2.84, dd (8.5, 4.9)	5.82, ddd (12.2, 8.5, 6.1)	3.82, d (6.1)	2.91, s	−24.3, t (28.1)
3b	H	H	Et	2.44, dd (11.0, 4.9)	2.86, dd (9.8, 4.9)	5.79, ddd (11.0, 9.8, 6.9)	3.83, d (6.9)	4.03, q, 0.67, t (7.3)	−24.3, t (28.1)
3c	H	H	^{n}Bu	2.40, dd (11.0, 4.9)	2.89, dd (7.9, 4.3)	5.71, ddd (11.0, 7.9 5.5)	3.84, d (5.5)	0.6–1.8, m	−24.2, t (28.1)
3d	H	H	Cy	2.20, dd (12.2, 4.9)	3.00, dd (7.4, 3.8)	5.63, ddd (12.2, 8.6, 6.1)	3.72, d (6.1)	0.8–1.9, m, 4.45, m	−24.4, t (28.8)
4	H	Me	Me	2.27, dd (11.0, 4.9)	2.86, dd (7.9, 4.9)	5.56, dd (11.0, 7.9)	1.26, d (3.7)	3.05, s	−23.6, t (28.1)
5a	Et	H	Me	2.55, m	0.8, t (7), 1.2, m	5.41, dd (11.0, 6.7)	3.60, d (6.7)	2.94, s	−24.4, dd (24.5, 25.6)
5b	Et	H	Cy	2.58, m	[a]	5.37, dd (9.8, 6.1)	3.72, d (6.1)	0.6–1.9, m, 4.46, m	−23.7, dd (24.5, 29.4)

[a] Signals are obscured by the large signals of Cy.

carbon adjacent to carbonyl group as a doublet at 59.0 ppm because of coupling with one P nucleus ($J = 13.8$ Hz), whereas the central carbon is observed as a singlet. Observation of a small coupling between carbonyl carbon and one of the P nuclei suggests the coordination of the carbonyl group to ruthenium *trans* to one PPh_3. ^{31}P NMR of **3a** shows an AB quartet pattern at 58.5 and 55.5 ppm from external PPh_3 with a coupling constant of 19 Hz, indicating that the two P ligands have essentially different magnetic circumstances. IR spectra of **3a–3d** show broad peaks at about 1936–2045 cm^{-1} assignable to ν(Ru–H). Carbonyl and C=C stretching bands for these complexes are unexpectedly weak and only broad peaks with medium intensity are observed at about 1440 cm^{-1}. The results suggest the coordination of carbonyl group with extensive delocalization along the π-allyl and carbonyl groups in these complexes, forming an anticonfiguration of the allylic moiety. A possible geometry of the complexes **3a–3d** was shown in eqn. 1. Unusual weakening of the carbonyl stretching bands in **3** due to chelation by the ester group has also been known in hydrido(2-n-butoxycarbonylpropenyl-C^1, O)tris(triphenylphosphine)ruthenium(II).

2.2. Reactions of 1 and 2 with other alkyl 2-alkenoates

When the reaction of **1** with alkyl 2-hexenoate was carried out in benzene at room temperature for 1 day, a mixture of $RuH(\eta^3\text{-}EtCHCHCHCOOR)(PPh_3)_2$ (R = Me (**5a**), Cy (**5b**)) and a tentatively assigned dienecarboxylate complex $Ru(MeCH{=}CHCH{=}CHCOOR)(PPh_3)_3$ (R = Me (**6a**), Cy (**6b**)) was obtained in about a 1:1 ratio. Methyl 2-pentenoate also reacted with **2** to give a similar dienecarboxylate complex **6c** in 12 h. Figure 1 demonstrates the time course of the gaseous products during the reaction of **1** with cyclohexyl 2-hexenoate. Evolution of ethylene gas took place in the initial 2 h period (60%) and then the ethylene in the gas phase was gradually hydrogenated to ethane (50%) in 24 h with concomitant transformation from **5b** to **6b**. Formation of the mono(dienecarboxylate)-ruthenium complexes **6a** and **6b** was tentatively confirmed by the ^1H NMR analysis of the product in the independent *in-situ* reaction of **2** with cyclohexyl 2,4-hexanedienoate (*vide infra*). In this case, evolution of only ethylene gas was observed. The formation of such a dienecarboxylate complex of ruthenium can be understood by assuming the formation of σ-allyl species such as **5′** in Scheme 1 from which β-hydride elimination takes place to give the product. The two hydrides formed in these process are considered to be consumed for the hydrogenation of ethylene. In the absence of ethylene **5b** can be stable towards β elimination. In fact, the pure π-allyl complex **5b** was obtained

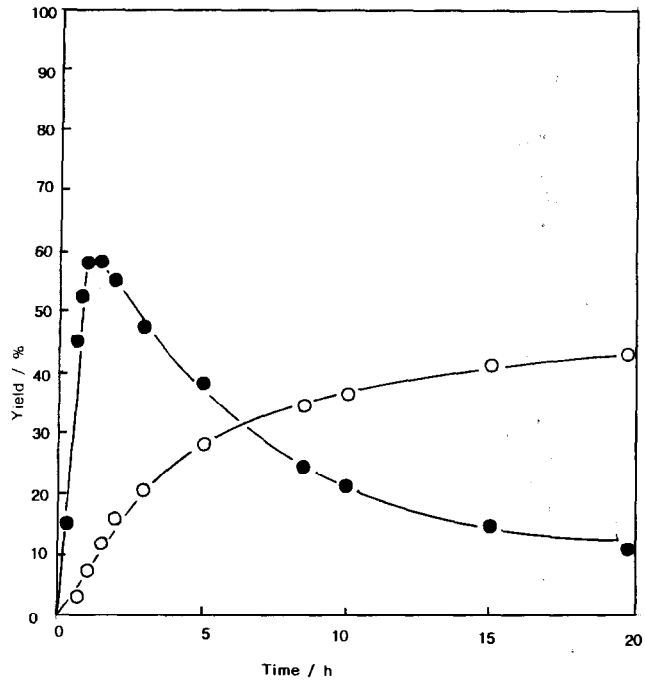
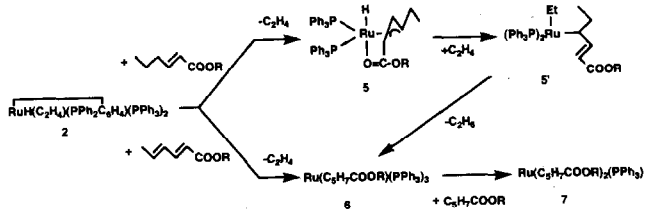


Fig. 1. Time–yield curve of ethylene and ethane for the reaction of **1** with cyclohexyl 2-hexenoate in benzene at room temperature (**1**, 0.141 mmol; cyclohexyl 2-hexenoate, 0.905 mmol; benzene; 2.0 ml): •, ethylene; ○, ethane.

by the independent reaction of **2** with cyclohexyl 2-hexenoate. However, bubbling of ethylene gas into a benzene solution of **5b** slowly gave **6b** accompanied by hydrogenation of ethylene.

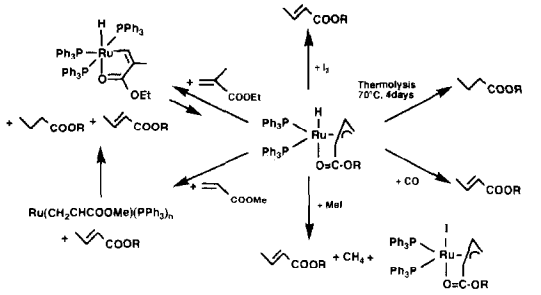
2.3. Reaction of 1 with cyclohexyl sorbate

As discussed above, dienecarboxylate ruthenium complexes were formed by the reaction of hydrido(π-allyl)ruthenium complexes with ethylene as well as by the reaction of **1** with alkyl 2-hexenoate. Isolation of these products in a pure form either from the reaction mixture or from the independent reaction of **2** with cyclohexyl sorbate has failed, since they are always obtained as mixtures of products. The NMR spectrum of the C_6D_6 solution containing **1** and cyclohexyl sorbate revealed the existence of at least two kinds of dienecarboxylate complex. However, when excess cy-



Scheme 1. A reaction mechanism of **2** with alkyl 2-hexenoate.

clohexyl sorbate was employed in the reaction, bis(cyclohexyl sorbate)(triphenylphosphine)ruthenium(0) (**7**) was isolated with the liberation of an equimolar amount of ethylene. Initial mono(dienecarboxylate)ruthenium complex (**6b**) is likely to contain three PPh_3 ligands to satisfy the 18 e rule, since a 1,3-butadiene complex $Ru(C_4H_6)(PPh_3)_3$ has been reported [2]. Thus the reactions of **1** or **2** with 1,3-butadiene gave both mono(butadiene)ruthenium(0) and/or bis(butadiene)ruthenium(0) complexes depending on the reaction conditions employed, in which the former contains three PPh_3 ligands.



Scheme 2. Reactions of $RuH(CH_2CHCHCOOR)(PPh_3)_2$.

2.4. Thermolysis and reactions of 3a

Thermolysis of **3a** was performed in benzene-d_6 at 70°C to liberate methyl butyrate with a 70% yield after a week. Reductive elimination and hydrogenation took place. The hydrogen source in the product may be triphenylphosphine ligands, since no deuterium atoms from the solvent were incorporated into the liberated ester, although the mechanism is not well understood at present.

2.5. Reactions of 3a with hydrogen, CO and MeI

The reaction of **3a** with hydrogen liberated methyl isobutyrate quantitatively. The resultant ruthenium complex is $RuH_4(PPh_3)_3$, as revealed by the ^1H NMR showing a broad signal of the hydride at -7.1 ppm as well as by the formation of $RuH_2(N_2)(PPh_3)_3$ on interaction with atmospheric nitrogen gas [10]. Introduction of carbon monoxide gas into a benzene solution of **3a** liberated methyl crotonate quantitatively in 2 h at room temperature. No carbonylation of the alkenecarboxylate was observed. Coordination of CO may induce the reductive elimination of methyl crotonate. The addition of iodine also accelerated the reductive elimination of methyl crotonate. Such an acceleration effect of electrophiles in the reductive elimination is well known [11]. The reaction of **3a** with methyl iodide liberated mainly methane in addition to a small amount of methyl crotonate. The ruthenium product is tentatively assigned as $RuI(CH_2CHCHCOOMe)(PPh_3)_2$ from the NMR spectrum of the residual solid. No methylation products of the ester were obtained. One possible mechanism for the reaction is the initial oxidative addition of methyl iodide to give a hydrido(methyl)(iodo)(π-allyl)Ru(IV) intermediate from which selective reductive elimination of methane took place. Reductive elimination including allyl entity may be slow in comparison with alkyl or hydride [12].

2.6. Reactions of 3a with alkenecarboxylates

Chemical reactivity of other alkenecarboxylates is summarized in Scheme 2. The reaction of **3a** with ethyl methacrylate slowly took place to liberate methyl crotonate with a 40% yield under ambient conditions in 1 week accompanied by partial decomposition of the complex. The ruthenium product was hydrido(2-ethoxycarbonylpropenyl-C^1,O)tris(triphenylphosphine)-ruthenium(II). Reverse reaction also took place if the temperature was raised to 70°C, resulting in the formation of **3a** with a 15% yield after 12 h. This indicates the reversibility of the reaction, although the rate is very slow. In contrast, no reaction of **3a** with ethylene took place. In the reaction of **3a** with a more electronegative olefin such as methyl acrylate, methyl crotonate was liberated in a few minutes. Coordination of methyl acrylate seems to facilitate the reductive elimination. The ruthenium products were not fully characterized but are considered to be methyl acrylate coordinated complexes of Ru. The reaction of **3a** with methyl tiglate also took place to liberate methyl crotonate at 70°C, although the rate is considerably slow. An analogous hydrido(allyl)ruthenium complex was formed with a low yield.

From these results, it can be concluded that the selectivity of the C–H bond activation of alkenecarboxylates by Ru(0) complex is highly dependent on the substrate employed. In particular, thermodynamic stability of the reaction products seems to determine the reaction pathway, although it is still ambiguous which will determine the regioselectivity of C–H bond cleavage. The C–H bond activation producing π-allylruthenium species is highly favoured in comparison with the formation of alkenylruthenium species, since alkyl crotonates having a β-C(sp^2)–H group afforded only π-allylruthenium complexes. The steric effect in the reaction is also important, since the reaction of **1** with methyl tiglate is not favoured. The failure of C–H bond cleavage in methyl acrylate may be due to the stability of the products such as methylacrylate coordinated ruthenium complexes. It is interesting to note that β-hydride elimination from the π-allyl intermediate takes place to give a dienecarboxylate complex, if hydride accepter such as ethylene exists.

2.7. Catalytic dimerization of benzaldehyde with 2a

Benzaldehyde in benzene was dimerized to benzyl benzoate with a 60% yield in 10 min in the presence of catalytic amount of **3a** (2 mol.%). After 10 h the yield increased to 82%. Similar Tischchenko-type dimerization of aldehydes is known to be catalysed by **1** or **2** and the mechanism including oxidative addition of benzaldehyde and insertion of benzaldehyde into ruthenium hydride bond followed by reductive elimination of benzyl benzoate has been proposed [13].

3. Experimental details

All manipulations were carried out under deoxygenated nitrogen or argon. Solvents such as benzene, toluene, ether, hexane and tetrahydrofuran were dried and distilled over benzophenone–ketyl under nitrogen and stored under nitrogen before use. $RuH(C_2H_4)(PPh_3)_2(PPh_2C_6H_4)$ (**1**) [2] and $RuH_2(PPh_3)_4$ (**2**) [14] were prepared by the methods given in the literature. Esters available from Tokyo Kasei Co. Ltd or Aldrich Chemicals were purchased and dried with calcium hydride. Cyclohexyl crotonate, cyclohexyl 2-hexenoate and cyclohexyl sorbate were prepared by the reactions of cyclohexanol with corresponding carboxylates in the presence of hydroquinone and methanesulfonic acid. IR spectra were recorded on Jasco A302 and FTIR 5 M spectrometers. NMR spectra were measured using JEOL NMR FX-200 and FX90Q spectrometers. Elemental analyses were performed with a Yanagimoto CHN autocorder type MT-2. Gases were quantitatively analysed either by gas chromatography (GC) using the internal standard method or by GC after the gases were collected with a Toepler pump, from which the gas volume was measured.

3.1. Hydrido(1-methoxycarbonyl-η^3-allyl-C^1, C^3)bis(triphenylphosphine)ruthenium(II) (3a)

Methyl crotonate (0.68 mmol) was introduced into a benzene solution of **1** (315.8 mg, 0.34 mmol) with a hypodermic syringe to give a brown homogeneous solution in 12 h. After removal of all the volatile matters, the residue was extracted with ether and filtered with short celite column. The solution was concentrated and the addition of hexane gave microcrystalline powder as a benzene adduct. ^1H NMR supports the inclusion of one molecule of benzene (yield, 184 mg (67%)). Anal. Found: C, 70.03; H, 5.30. $C_{47}H_{44}O_2P_2Ru$ calc.: C, 70.22; H, 5.52%. IR: ν(Ru–H) 1937m, 1440vw cm^{-1}. ^1H NMR: see Table 1. ^{13}C NMR (C_6D_6, room temperature): 50.3 (s, OMe), 56.3 (dd, $J = 3.2$, 20.6 Hz, CH_2), 59.0 (d, $J = 13.8$ Hz, $CHCO$), 97.6 (s, CH_2CH–), 127.3, 127.4, 127.8, 128.4, 128.6, 128.8, 131.5, 132.2, 132.4, 134.0, 134.2, 134.3, 134.5 (PPh_3), 168.3 (d, $J = 1.8$ Hz, C=O) ppm (with respect to tetramethylsilane). ^{31}P NMR (toluene-d_8, room temperature): 58.5 (d, $J = 19$ Hz), 66.6 (d, $J = 19$ Hz) ppm (with respect to external PPh_3). The reaction of **2** (1.09 g, 0.946 mmol) with methyl crotonate (9.46 mmol) in benzene also gave the same compounds. In order to obtain the pure compound, purification by column chromatography using neutral alumina Super 1 was performed (yield, 20%). The observed low yield in comparison with the former method may be due to loss of the product during purification.

3.2. Reaction of 1 and 2 with methyl 3-butenoate

The reaction of **1** (46.0 mg, 0.0390 mmol) with methyl 3-butenoate (0.374 mmol) in benzene at room temperature for 12 h was performed and the work-up gave **3a** (8.9 mg; 18%), which was revealed by IR and ^1H NMR spectroscopy. **2** (48.8 mg, 0.0424 mmol) also reacted with methyl 3-butenoate (0.56 mmol) to give **3a** (18.4 mg; 35%). During the reaction, complete isomerization of methyl 3-butenoate to methyl crotonate was observed in both cases.

The rates of the isomerization of methyl crotonate and formation of **3a** in the reaction of **1** (26.8 mg, 0.0293 mmol) with methyl crotonate (0.0585 mmol) in toluene-d_8 was followed by ^1H NMR at 10°C. Both half-lives were approximately the same (about 40 min).

3.3. Hydrido(1-cyclohexyloxycarbonyl-η^3-allyl-C^1,C^3)bis(triphenylphosphine)ruthenium(II) (3d)

To a benzene solution of **1** (319 mg, 0.348 mmol), cyclohexyl crotonate (1.14 mmol) was added and stirred for 39 h at room temperature to give a red homogeneous solution. After removal of the solvent, the residual solid was recrystallized from an ether–hexane mixture to give pale yellow crystals of **3d** (yield, 75 mg (27%)). Anal. Found: 69.59; H, 5.84. $C_{46}H_{46}O_2P_2Ru$ calc.: 69.09; H, 5.66%. IR: ν(Ru–H) 2045 cm^{-1}. Reaction of **2** (117.4 mg, 0.102 mmol) with cyclohexyl crotonate (0.240 mmol) in toluene at room temperature for 2 days also gave the same complex. In solution, cyclohexyl butyrate (0.0740 mmol; 73% per Ru) was detected.

Similar reactions of **1** (73.8 mg, 0.0806 mmol) with ethyl crotonate (0.16 mmol) and of **1** (51.1 mg, 0.0558 mmol) with *n*-butyl crotonate (0.12 mmol) in benzene gave the analogous complexes **3b** (35%) and **3c** (32%) which are characterized only spectroscopically. IR: ν(Ru–H) **3b**, 1960 cm^{-1}; **3c**, 1960 cm^{-1}. The ^1H NMR data of **3a–3d** are summarized in Table 1.

3.4. Reaction of 1 with cyclohexyl 2-hexenoate

1 (406.1 mg, 0.443 mmol) in benzene was reacted with cyclohexyl 2-hexenoate (1.13 mmol) at 40°C for 6

h. Ethylene (0.06 mmol) and ethane (0.21 mmol) were detected in the gas phase. After evaporating the solvent, the residue was extracted with ether, and hexane was added to separate a yellow solid (yield, 251 mg). ^{1}H NMR of the product indicates the formation of a mixture of **5b** and a dienecarboxylate complex **6b** in about a 1:1 ratio. ^{1}H NMR for **6b**: −0.2, 0.1, 5.2, 6.3 (m, CH), 0.6–2.0 (m, Me, Cy), 6.8–7.9 (m, PPh_3) ppm. The ^{1}H NMR data for **5b** are summarized in Table 1.

*3.5. Reactions of **1** with methyl 2-hexenoate and 2-pentenoate*

An NMR tube reaction between **1** (15.6 mg, 0.017 mmol) and methyl 2-hexenoate (0.0340 mmol) in C_6D_6 was performed at room temperature. After 1 h, **5a** was detected in ^{1}H NMR (see Table 1 for NMR data) with about a 50% yield. Further reaction for 28 h resulted in the formation of a mixture of **5a** and a dienecarboxylate complex **6a** in about a 1:1 ratio. The reaction of **1** (135.7 mg, 0.148 mmol) with methyl 2-pentenoate (0.295 mmol) in benzene for 12 h also gave a mixture of **5c** and a corresponding dienecarboxylate complex **6c** (36.2 mg; 25%). ^{1}H NMR (C_6D_6) for **6a**: −0.27, 1.94, 4.62, 6.22 (m, CH), 3.43 (s, OMe), 1.0 (m, Me), 6.7–7.9 (m, PPh_3) ppm. ^{1}H NMR for **6c**: −0.91, 1.67, 3.17, 5.22, 6.47 (br, CH_2=CHCH=CH–), 3.47 (s, OMe), 6.7–7.7 (m, PPh_3) ppm.

*3.6. Hydrido(1-cyclohexyloxycarbonyl-3-ethyl-η^3-allyl-C^1,C^3)bis(triphenylphosphine)ruthenium(II) (**5b**)*

To a benzene solution of **2** (423 mg, 0.368 mmol), cyclohexyl 2-hexenoate (1.13 mmol) was added and stirred for 70 h at room temperature to give a homogeneous red solution. The addition of hexane to the concentrated solution gave an orange solid which was recrystallized from an ether–hexane mixture to give orange crystals of **5b** (yield, 123 mg (41%)). IR: ν(C=O) 1683; ν(C–O) 1160 cm^{-1}. The ^{1}H NMR data are shown in Table 1.

When **5b** (5.6 mg, 0.0068 mmol) was brought into contact with ethylene (1 atm) in benzene at room temperature, ethane gas gradually formed. After 2 h, **6b** (about 30%) was detected by ^{1}H NMR. Other unidentified products also formed. ^{1}H NMR for **6b**: −0.2, 0.1, 5.2, 6.3 (m, CH), 0.6–2.0 (m, Me, Cy), 6.8–7.9 (m, PPh_3) ppm.

3.7. Bis(cyclohexyl sorbate)(triphenylphosphine)ruthenium(0) (7)

To a benzene solution of **1** (195 mg, 0.213 mmol), excess cyclohexyl sorbate (0.670 mmol) was added and the solution was stirred for 1 day at room temperature. After removal of volatile matter *in vacuo*, the brown residue was extracted with hexane. Concentration and cooling of the solution gave yellow crystals (yield, 25 mg (16%)). Anal. Found: 66.45; H, 6.86. $C_{42}H_{51}O_4PRu$ calc.: 67.09; H, 6.83%. IR: ν(CO) 1683 cm^{-1}. ^{1}H NMR (C_6D_6): 0.3, 2.0, 5.0, 5.6 (br, 2H each, CH), 1.0 (d, J = 7 Hz, 6H, Me), 1.1–1.9 (m, 20H, Cy), 4.9 (m, 2H, PCH), 7.0–7.3, 7.8–8.0 (m, 15H, Ph) ppm.

^{1}H NMR of a C_6D_6 solution containing **1** (23.0 mg, 0.025 mmol) and cyclohexyl sorbate (0.0479 mmol) at room temperature showed the presence of complexes **6a** and **7** in about a 1:1 ratio. Isolation of mono(diene carboxylate) complexes **6a**–**6c** either from the above reaction of **1** with dienecarboxylates or by the reactions of **1** with alkyl hexenoate and alkyl pentenoate failed. They were always obtained as a mixture of products containing **6**, **7** (or **3**) and uncharacterizable materials but are tentatively formulated as Ru(dienecarboxylate)(PPh_3)$_3$ by the NMR result as well as by the fact that **1** gives a similar 1,3-butadiene complex having three PPh_3 ligands [2].

*3.8. Thermolysis of **3a** and **3d***

A C_6D_6 solution of **3a** (10 mg, 0.014 mmol) was heated at 70°C for 1 week. The formation of methyl butyrate (46%) was confirmed by NMR. **3d** (10 mg, 0.013 mmol) was not decomposed at 70°C for 7 h and remained intact.

*3.9. Reaction of **3a** with H_2*

3a (7.5 mg, 0.0103 mmol) in C_6D_6 was brought into contact with 1 atm of hydrogen at room temperature for 12 h. A quantitative yield (100%) of methyl butyrate was detected. ^{1}H NMR of the solution showed a broad hydride signal at −7.1 ppm assignable to $RuH_4(PPh_3)_3$. After removal of the solvent the product was isolated under nitrogen. The IR spectrum of the product shows a ν(N≡N) band at 2142 cm^{-1} for $RuH_2(N_2)(PPh_3)_3$. **3d** also reacted with hydrogen similarly.

*3.10. Reaction of **3a** with CO*

Carbon monoxide (1 atm) was introduced into a C_6D_6 solution of **1** (10 mg, 0.014 mmol) at room temperature. After 8 h, methyl crotonate (99%) was detected by NMR. **3d** also liberated cyclohexyl crotonate quantitatively on interaction with CO.

*3.11. Reaction of **3a** with MeI*

To a C_6D_6 solution of **3a** (12.6 mg, 0.0173 mmol) was added methyl iodide (0.346 mmol) at room temperature. After 2 days, methane (58%), ethane (0.9%) and methyl crotonate (21.5%) were detected by GC. ^{1}H NMR of the resultant solid after evaporating all volatile matters shows that four protons assignable to a methoxycarbonyl-π-allyl moiety were observed at 1.87

(d, $J = 11.0$ Hz), 2.15 (d, $J = 7.2$ Hz), 4.48 (ddd, $J =$ 11.0, 7.2, 6.1 Hz) and 4.7 (d, $J = 6.1$ Hz) ppm and an OMe signal at 3.42 (s) ppm, suggesting the formation of $RuI(CH_2CHCHCOOMe)(PPh_3)_2$.

*3.12. Reaction of **3a** with iodine*

1 (10 mg, 0.014 mmol) in C_6D_6 was reacted with iodine (0.028 mmol) to give a deep-brown solution. After 8 h the formation of methyl crotonate was confirmed by ^1H NMR. Other unidentified products were also formed.

*3.13. Dimerization of benzaldehyde with **3a***

Benzaldehyde (1.32 mmol) was added to a benzene solution of **3a** (19.2 mg, 0.0263 mmol) at room temperature. After 10 min, benzyl benzoate was detected with a 60% yield based on the mole of benzaldehyde used. The yield increased to 82% after 10 h.

*3.14. Reaction of **3a** with ethyl methacrylate*

To a C_6D_6 solution of **3a** (13.6 mg, 0.188 mmol) was added ethyl methacrylate (0.188 mmol) at room temperature. After 58 h, a mixture of **3a** and hydrido(2-ethoxycarbonylpropenyl-C^1,O)tris(triphenylphosphine)-ruthenium was formed in a 1:3 ratio. After a week the latter complex was formed with a 60% yield accompanied by decomposition of **3a**, liberating methyl crotonate (40%).

The reverse reaction of hydrido(2-ethoxycarbonylpropenyl-C^1,O)tris(triphenylphosphine)ruthenium (10.9 mg, 0.0109 mmol) with methyl crotonate (0.0109 mmol) in C_6D_6 at 70°C for 12 h gave **3a** (15%) and ethyl methacrylate (20%).

*3.15. Reaction of **3a** with methyl acrylate*

To a C_6D_6 solution of **3a** (27.2 mg, 0.297 mmol) was added methyl acrylate (0.0297 mmol) at room temperature. After 1 h, **3a** was completely converted to liberate methyl crotonate with a 80% yield. The ^1H NMR spectrum of the product after work-up is the same as that of product obtained from the reaction of **2** (27.2 mg, 0.0297 mmol) with methyl acrylate (0.0297 mmol). ^1H NMR: 2.5, 3.1, 4.3 (br, $CH{=}CH_2$), 3.66 (s, OMe), 6.8–7.8 (m, PPh_3) ppm. IR: ν(C=O) 1691 cm^{-1}. The addition of methyl crotonate (0.297 mmol) to this NMR sample did not give **3a**.

*3.16. Reaction of **3a** with methyl tiglate*

To a C_6D_6 solution of **3a** (12.9 mg, 0.178 mmol) was added methyl tiglate (0.0178 mmol). No reaction took place after 59 h at room temperature. A similar reaction at 70°C for 10 h resulted in 30% conversion to liberate methyl butyrate (5%) and hydrido(1-methyl-2-ethoxycarbonylpropenyl-C^1,O)tris(triphenylphosphine)-ruthenium (8%) which is tentatively assigned by NMR (Table 1).

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