Synthesis of Some [1,2-Bis(alkoxycarbonyl)ethyl]ruthenium(II) Complexes and Their Catalytic Activities for *cis-trans* Isomerization of Dialkyl Maleates

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The hydridoruthenium(II) complex $[RuCl(CO)H(PPh_3)_3]$ (**1**) reacted smoothly with dimethyl maleate and diethyl maleate at room temperature to give insertion products, $[Ru\{CH(CO_2R)CH_2C(O)OR\}Cl(CO)(PPh_3)_2]$ (**2**; R = Me) and (**3**; R = Et), respectively. Complex (**2**) was also formed by reaction of (**1**) with dimethyl fumarate. Complexes (**2**) and (**3**) were converted into binuclear complexes $[\{Ru[CH(CO_2R)CH_2C(O)OR](\mu\text{-}Cl)(CO)(PPh_3)\}_2]$ (**4**; R = Me) and (**5**; R = Et), respectively, by heating above 100 °C. Complex (**4**) reacted with $Na[BH(pz)_3]$(pz = 1-pyrazolyl) at ambient temperature to afford $[Ru\{CH(CO_2Me)CH_2CO_2Me\}(CO)\{BH(pz)_3\}(PPh_3)]$. Complexes (**1**), (**2**), and (**4**) were found to catalyze *cis-trans* isomerization of dialkyl maleates above 100 °C. A kinetic study of the isomerization of dimethyl maleate revealed that the reaction rates were proportional to the concentrations of both the substrate and the catalyst, and that the ratio of the catalytic constants per ruthenium atom is about 1.6:1.0:0.36 for (**1**), (**2**), and (**4**), respectively, at 120 °C. Addition of PPh_3 to the catalyst accelerated the reaction rates. It is deduced that the isomerization proceeds through an insertion–β-elimination mechanism.

It has been reported that ruthenium complexes catalyze the isomerization, hydrogenation, and transfer hydrogenation of olefins.[1,2] These catalytic reactions involve insertion of the unsaturated substrates into a hydrido–ruthenium bond as an elementary process.[1,2]

We reported previously that a hydridoruthenium(II) complex, $[RuCl(CO)H(PPh_3)_3]$ (**1**) reacted with 2-acylpyridines,[3] vinyl compounds,[4,5] and conjugated dienes[5] to give the corresponding insertion products. As discussed previously,[5] the reactivity of (**1**) is a little lower than that of $[RuH_2(PPh_3)_4]$. However, (**1**) is still a versatile complex for the study of insertion reactions since it gave isolable insertion products with olefinic compounds[4,5] as well as those with various unsaturated compounds,[3,6–8] whereas the insertion products of $[RuH_2(PPh_3)_4]$ gave rise to subsequent reactions, *e.g.* polymerization,[9] reductive elimination,[10,11] or interligand hydrogen transfer.[11]

In this paper, we will deal with the insertion reactions of dialkyl maleates and fumarate into complex (**1**) and *cis-trans* isomerisation of dialkyl maleates catalyzed by (**1**) or two [1,2-bis(methoxycarbonyl)ethyl]ruthenium(II) complexes derived from (**1**).

Experimental

The starting ruthenium complex (**1**)[12] and sodium hydrotris(1-pyrazolyl)borate,[13] $Na[BH(pz)_3]$, were prepared according to literature methods. Solvents were purified by usual methods and stored under dry nitrogen. The other reagents were commercially available and used without further purification. Reactions were carried out under dry nitrogen, although manipulations and separatory procedures were generally carried out in air.

I.r. spectra were recorded on a JASCO A-100 spectrophotometer, ^1H, ^{13}C, and ^{31}P n.m.r. spectra on a JEOL model JNM GX-400 spectrometer at 400.0, 100.6, and 161.9 MHz, respectively. For the ^{31}P n.m.r. spectra an 85% H_3PO_4 solution was used as an external standard. Melting points were measured in capillary tubes on a Yanagimoto MP-S3 microstage apparatus and are uncorrected. Molecular weights were obtained in a 1,2-dichloroethane solution by use of a Corona Denki model 114 molecular-weight apparatus.

Synthesis of [1,2-*Bis*(*alkoxycarbonyl*)*ethyl*-C^1,O]*carbonylchlorobis*(*triphenylphosphine*)*ruthenium*(II) (**2**) *and* (**3**).—A tetrahydrofuran (thf) suspension (40 cm^3) containing complex (**1**) (1.00 g, 1.04 mmol) and dimethyl maleate (0.76 g, 5.2 mmol) was stirred at room temperature for 16 h. The reaction mixture was filtered and concentrated to *ca.* 15 cm^3 under reduced pressure. The resulting solution was diluted with hexane to give a greenish yellow powder, $[Ru\{CH(CO_2Me)CH_2C(O)OMe\}Cl(CO)(PPh_3)_2]$ (**2**). Yield: 660 mg, 77%. M.p. 189 °C (Found: C, 62.4; H, 5.1. $C_{39}H_{39}ClO_5P_2Ru$ requires C, 61.9; H, 4.7%).

Complex (**1**) reacted with dimethyl fumarate similarly to afford (**2**) in an analogous yield to the case of dimethyl maleate.

Treatment of (**1**) with diethyl maleate in thf, followed by a similar procedure to the case of (**2**), gave a greenish yellow powder, $[Ru\{CH(CO_2Et)CH_2C(O)OEt\}Cl(CO)(PPh_3)_2]$ (**3**). Yield 88% M.p. 195—199 °C (decomp.).

Thermolysis of Complex (**2**).—A dioxane suspension (15 cm^3) containing complex (**2**) (0.50 g, 0.52 mmol) was refluxed for 15 h. After the solvent was evaporated under reduced pressure, the residue was chromatographed on a silica gel column 200 × 12 mm). The yellow fraction eluted with dichloromethane–diethyl ether (1:1) was concentrated and diluted with hexane to give a yellow powder, $[\{Ru[CH(CO_2Me)CH_2C(O)OMe](\mu\text{-}Cl)(CO)(PPh_3)\}_2]$ (**4**). Yield 40%. M.p. 176—181 °C (Found: C, 52.0; H, 4.3%; *M* 1 130. $C_{50}H_{48}Cl_2O_{10}P_2Ru_2$ requires C, 51.9; H, 4.2%; *M* 1 143.9).

Preparation of Di-μ-*chloro-bis*{[1,2-(*bis-ethoxycarbonyl*)*ethyl*-C^1,O]*carbonyl*(*triphenylphosphine*)*ruthenium*(II)} (**5**).—A toluene suspension (20 cm^3) containing complex (**3**) (0.14 g, 0.16 mmol) was refluxed for 5 h. After the solvent was evaporated under reduced pressure, the residue was recrystallized from

Table 1. Proton n.m.r. data for the ruthenium complexes[a]

	RuCH		CHCH$_2$		CH$_3$	Other	
Complex	δ	J(HH)	δ	J(HH)	δ	δ[b]	J(HH)
(2)	2.86 (dt)[c]	8	2.73 (dd)	17.6, 8.3	3.11 (s)	—	
			3.48 (dd)	17.6	3.42 (s)		
(3)	2.76 (dt)[d]	8.6	2.68 (dd)	16.8, 8.2	0.94 (t)[e]	3.44 (Aq, 1 H, OCH$_2$)	10.6, 7.2
			3.47 (dd)	16.3, 7.0	0.97 (t)[e]	3.51 (Bq, 1 H, OCH$_2$)	11.0, 7.2
						3.87 (A′q, 1 H, OCH$_2$)	10.6, 7.2
						4.11 (B′q, 1 H, OCH$_2$)	10.6, 7.2
(4)	2.43 (t)	7	2.05 (dd)	18.5, 7.5	3.50 (s)	—	
	2.45 (t)	7	2.16 (dd)	18.9, 7.5	3.62 (s)		
			3.27 (dd)	18.5, 7.0	3.74 (s)		
			3.47 (dd)	18.9, —	3.80 (s)		
(5)	2.47 (t)	7	2.05 (dd)	18.7, 7.2	1.18 (t)[e]	3.90 (Aq, 1.1 H, OCH$_2$)	11.0, 7.0
	2.49 (t)	7	2.09 (dd)	18.7, 7.2	1.25 (t)[e]	3.96 (A′ + A″, q, 2 H, OCH$_2$)	10.6, 7.2
			3.27 (dd)	18.7, 7.2	1.28 (t)[e]	4.01 (B′q, 1.1 H, OCH$_2$)	11.5, 7.2
			3.42 (dd)	18.7, 7.2	1.30 (t)[e]	4.09 (A″q, 0.9 H, OCH$_2$)	10.0, 7.3
						4.10 (B″q, 0.9 H, OCH$_2$)	— 7.0
						4.40 (B″q, 0.9 H, OCH$_2$)	10.6, 7.0
						4.48 (Bq, 1.1 H, OCH$_2$)	10.6, 7.0
(6)	0.70 (br)	—	2.50 (m)	—	3.24 (s)	5.70 (t, 1 H, H^4 of pz)	2.0
					3.42 (s)	6.03 (t, 1 H, H^4 of pz)	2.0
						6.13 (br t, 1 H, H^4 of pz)	2.0
						6.57 (d, 1 H, H^3 of pz)	2.0
						6.78 (d, 1 H, H^3 of pz)	2.0
						7.24 (d, 1 H, H^3 of pz)	2.0
						7.53 (d, 1 H, H^5 of pz)	2.0
						7.79 (d, 1 H, H^5 of pz)	2.0
						8.13 (br, 1 H, H^5 of pz)	—

[a] In CDCl$_3$. [b] Signal shape, intensity, and assignment are given in the parentheses; A + B, A′ + B′, *etc.* represent pairs of the AB type quartet. [c] ^3J(CP) 3 Hz. [d] ^3J(CP) 3.3 Hz. [e] ^3J(HH) is about 7 Hz. See the J(HH) value of the neighbouring methylene group.

dichloromethane and hexane to give a dark yellow powder, [{$\overline{\text{Ru[CH(CO}_2\text{Et)CH}_2\text{C(O}}$)OEt](μ-Cl)(CO)(PPh$_3$)}$_2$] **(5)**. Yield 95%. M.p. 170 °C (decomp) (Found: C, 53.1, H, 4.5. $C_{54}H_{56}Cl_2O_{10}P_2Ru_2$ requires C, 54.0, H, 4.7%).

Synthesis of [*1,2-bis(methoxycarbonyl)ethyl*]*carbonyl*[*hydrotris(1-pyrazolyl)borato*](*triphenylphosphine*)*ruthenium*(II) **(6)**.—A thf suspension (15 cm^3) of complex **(4)** (0.28 g, 0.24 mmol) and sodium hydrotris(1-pyrazolyl)borate (0.10 g, 0.42 mmol) was stirred at room temperature for 48 h. The reaction mixture was injected on a silica gel column. A pale yellow fraction eluted with benzene–dichloromethane (1:5) was collected and evaporated to dryness. The residue was recrystallized from dichloromethane–hexane to give a pale yellow solid, **(6)**. Yield 0.18 g, 61%. M.p. 228—231 °C (Found: C, 54.1; H, 4.6; N, 11.1. $C_{34}H_{34}BN_6O_5PRu$ requires C, 54.5; H, 4.6; N, 11.2%).

Catalytic cis-trans *Isomerization of Dimethyl Maleate*.—*m*-Xylene (3.0 cm^3), dimethyl maleate (150 mg, 1.04 mmol) and a predetermined amount of catalyst were placed in a J-type glass tube, equipped with a silicone rubber stopper and purged with dry nitrogen. The tube was set at a constant position in a silicone oil-bath, heated at a constant temperature to (±0.1 °C). At predetermined times, 2.0×10^{-3} cm^3 of the reaction mixture was sampled by a microsyringe through the silicone rubber stopper and analyzed by gas–liquid chromatography: column, Apiezon Grease L; 130 °C.

Results and Discussion

[*1,2-Bis(alkoxycarbonyl)ethyl*]*carbonylchlorobis(triphenylphosphine)ruthenium*(II) *Complexes*, **(2)** *and* **(3)**.—The hydridoruthenium(II) complex **(1)** reacted readily with dimethyl maleate as well as with dimethyl fumarate in thf at room temperature to give an insertion product, [$\overline{\text{Ru\{CH(CO}_2\text{Me)CH}_2\text{C(O}}$)OMe}Cl(CO)(PPh$_3$)$_2$] **(2)**. The i.r. spectrum of **(2)** lacked the ν(Ru–H) band near 2 000 cm^{-1} observed for the starting complex **(1)**.[12] Complex **(2)** showed a very strong band at 1 932 cm^{-1}, ascribed to a terminal metal-bonded carbonyl group, and three strong bands at 1 085, 1 430, and 1 480 cm^{-1}, due to PPh$_3$ ligands. Furthermore, **(2)** exhibited two strong bands at 1 680 and 1 633 cm^{-1}. The former band was ascribed to a free ester carbonyl group and the latter to a metal-co-ordinated ester carbonyl, since it is well established that ν(C=O) for a ester group decreases on co-ordination to a metal.[5,14,15] This implies that dimethyl maleate or dimethyl fumarate has been inserted into the H–Ru bond of **(1)** to form a 1,2-bis(methoxycarbonyl)ethyl moiety, which serves as a five-membered C^1,O-chelating ligand in a similar fashion to a 2-(methoxycarbonyl)ethyl moiety, formed by the insertion of methyl acrylate into **(1)**.[5]

The ^{1}H n.m.r. spectrum of complex **(2)** showed two singlets at δ 3.11 and 3.42 (each, 3 H), due to methoxy protons. The ^{13}C-{^{1}H} n.m.r. spectrum exhibited two singlets at δ 49.7 and 53.8, attributable to methoxy methyl carbons. These and other n.m.r. data indicate that **(2)** consists of only one component.* The ruthenium-bonded carbon resonated as a double doublet at δ 32.0 p.p.m. [^2J(CP) 57.4 and 6.1 Hz]. The larger and the smaller coupling constants were ascribed to a *trans* and a *cis* coupling with ^{31}P nuclei, respectively. In addition, carbons of the unco-ordinated ester group and the co-ordinated one resonated as doublets at δ 184.2 [^3J(CP) 3.7] and 191.4 p.p.m. [^3J(CP) 11.0 Hz], respectively. Though the latter coupling is not so large, it shows that the co-ordinated ester carbonyl is situated *trans* to

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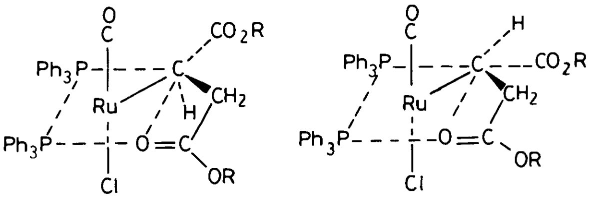
* Previously,[16] complex **(2)** was erroneously ascribed to a mixture of two isomeric insertion products.

Table 2. $^{13}C-\{^1H\}$ N.m.r. data for the ruthenium complexes.[a]

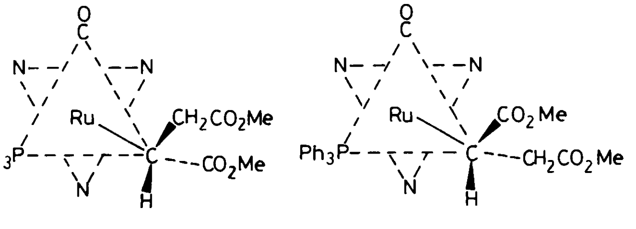
	RuCH		CH_2	CO_2		RuCO		CH_3	Other[b]
Complex	δ	J(CP)/Hz	δ	δ	J(CP)/Hz	δ	J(CP)/Hz	δ	δ
(2)	32.0 (dd)	57.4, 6.1	39.6 (d)[c]	184.2 (d)	3.7	202.3 (dd)	13.4	49.7	—
				191.4 (d)	11		12.2	53.8	
(3)	32.7 (dd)	56.8, 5.9	40.0 (d)[d]	184.1 (d)	3.9	202.6 (dd)	15.6	13.9	58.6 (OCH_2)
				191.2 (d)	11.8		12.7		63.3 (OCH_2)
(4)	17.9 (d)	7.3	37.9	182.2		206.7 (d)	9.8	50.2	—
	18.5 (d)	4.9	38.0	182.4		206.9 (d)	9.8	50.4	
				187.8				54.1	
				188.0				54.4	
(5)	17.7 (br)	—	34.1	176.4		—	—	14.0	58.6 (OCH_2)
	18.9 (br)	—	38.1	177.9				14.1	59.0 (OCH_2)
				181.8				14.5	63.3 (OCH_2)
				183.7					63.6 (OCH_2)
(6)	15.9 (d)	5.9	36.4	175.4		206.0 (d)	15.9	48.9	105.4 (C^4 of pz)
				184.9				50.7	105.8 (C^4 of pz)
									130.8 (C^3 of pz)
									132.7 (C^3 of pz)
									135.8 (C^3 of pz)
									142.5 (C^5 of pz)
									144.0 (C^5 of pz)
									144.3 (C^5 of pz)

[a] In $CDCl_3$, singlet, unless noted in parentheses. [b] Assignment is given in parentheses. [c] ^3J(CP) 3.7 Hz. [d] ^3J(CP) 3.9 Hz.



(A) **(B)**

Figure 1. Possible structures for complexes (**2**; R = Me) and (**3**; R = Et)



(C) **(D)**

Figure 2. Possible structures for complex (**6**); N represents the co-ordinated pyrazolyl group

one PPh_3 ligand. The $^{31}P-\{^1H\}$ n.m.r. spectrum exhibited two doublets at δ 21.74 and 47.83 p.p.m. [^2J(PP) 15.36 Hz], revealing that the two PPh_3 ligands are co-ordinated to ruthenium at mutually *cis* positions. On the basis of these data it is concluded that the 1,2-bis(methoxycarbonyl)ethyl moiety in (**2**) is co-ordinated to ruthenium *trans* to the two PPh_3 ligands. This is supported by the fact that the metal-bonded carbonyl carbon shows two small couplings with the two phosphorus atoms [^2J(CP) 13.4 and 12.2 Hz], resonating as a double doublet at δ 202.3 p.p.m. It is noteworthy that the two PPh_3 ligands in (**2**) are co-ordinated in *cis* arrangement, presenting a sharp contrast to the two *trans* PPh_3 ligands in $[Ru\{CH_2CH_2C(O)OMe\}Cl(CO)(PPh_3)_2]$, which was formed by the insertion of methyl acrylate into (**1**).[5] It seems that the ester group attached to the metal-bonded atom (C^1) in (**2**) prevents the two PPh_3 ligands from being co-ordinated at *trans* positions. The remaining carbonyl and chloro ligands are situated *trans* to each other. There are two possible structures (**A**) and (**B**) for complex (**2**) (Figure 1). Considering the relative bulkiness of these two ligands, (**2**) is ascribed to (**A**), in which the smaller carbonyl ligand is co-ordinated at the near side of the free ester group attached to the ruthenium-bonded methine carbon.

Complex (**3**), the ethyl homologue of (**2**), showed highly similar patterns of the ^1H and $^{13}C-\{^1H\}$ n.m.r. spectra to those of (**2**). It is noted that the methylene protons of both the co-ordinated and unco-ordinated ester groups resonated as two pairs of AB type quartets, each of which further splits into a quartet due to coupling with the neighbouring methyl protons. This indicates that the methylene protons are diastereotopic owing to the lack of free rotation of the methylene groups.

The $BH(pz)_3$ *Complex* (**6**).—The i.r. spectrum of complex (**6**) showed two bands at 1 735 and 1 680 cm^{-1}, attributable to free ester carbonyl stretching frequencies, in addition to seven bands at 2 495, 1 410, 1 308, 1 210, 1 120, 1 045, and 985 cm^{-1} characteristic of the $BH(pz)_3$ ligand.[13] These data indicate that the tridentate $BH(pz)_3$ ligand is co-ordinated to the ruthenium atom in a facial mode,[13] so as to leave the two ester carbonyl groups free. Complex (**6**) has two asymmetric centres, the central ruthenium atom and the ruthenium-bonded carbon. Then, two diastereomers (**C**) and (**D**) are possible, as in Figure 2. However, the ^1H and $^{13}C-\{^1H\}$ n.m.r. spectra exhibited one set of signals, as shown in Tables 1 and 2, implying that complex (**6**) is composed of only one component. This indicates that the stereochemistry of the 1-carbon is retained in the reaction course from (**2**) to (**6**) *via* (**4**). Thus (**6**) was assigned to structure (**C**).

The Dimeric Complexes (**4**) *and* (**5**).—Upon heating (**2**) above 100 °C a dimeric complex (**4**) was formed. The i.r. spectrum of (**4**) showed two strong absorption bands at 1 695 and 1 645 cm^{-1} and a shoulder near 1 655 cm^{-1}, indicating it has both free and co-ordinated ester carbonyl groups. Considering its molecular weight and elemental analyses, (**4**) is formulated as $[\{Ru[CH(CO_2Me)CH_2C(O)OMe]Cl(CO)(PPh_3)\}_2]$. The ^1H

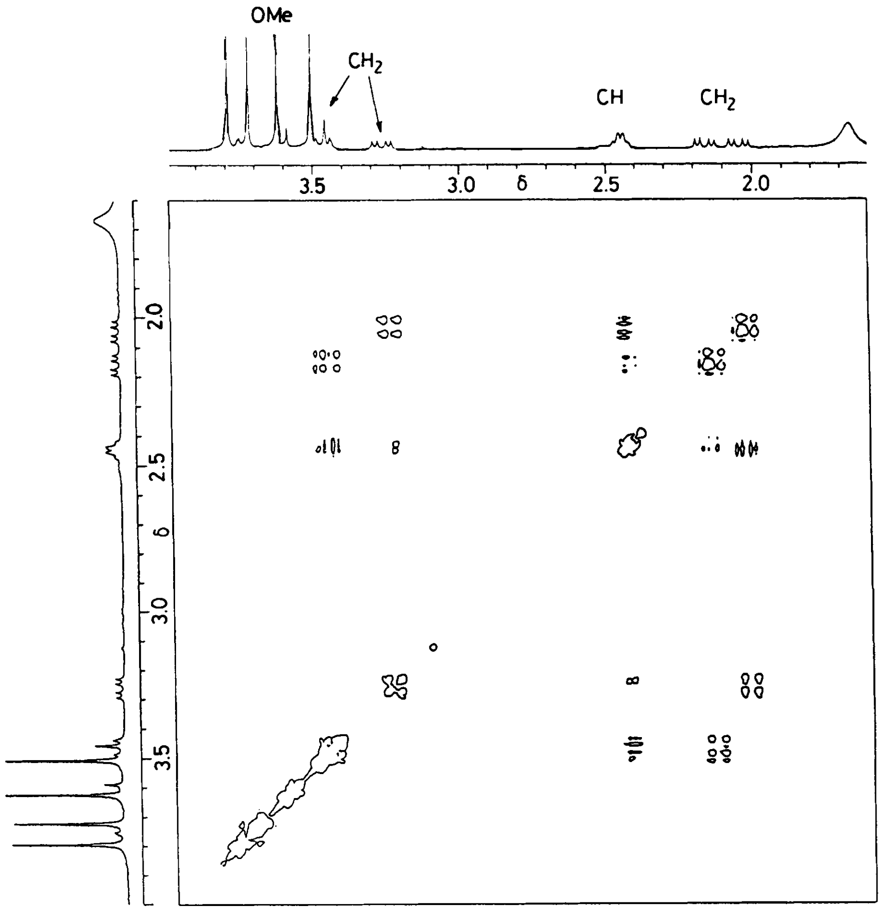


Figure 3. The $^{1}H-^{1}H$ COSY spectrum of complex (4)

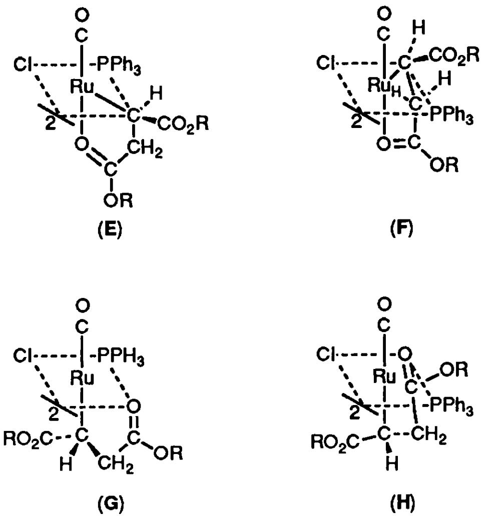


Figure 4. Possible structures for the monomeric unit of complexes (4; R = Me) and (5; R = Et)

n.m.r. spectrum of (4) exhibited four sharp singlets at δ 3.50, 3.62, 3.74, and 3.80, characteristic of methoxy protons. The ruthenium-bonded methine proton and the methylene protons were assigned on the basis of $^{1}H-^{1}H$ (Figure 3) and $^{1}H-^{13}C$ correlation spectroscopy (COSY). In the former COSY spectrum a triplet at δ 2.45 correlated with two double doublets at δ 2.05 and 3.27, whereas a triplet at δ 2.43 correlated with two double doublets at δ 2.16 and 3.47, the latter of which was partly overlapped with the methoxy signal at δ 3.50. These data indicate clearly that (4) has two sets of $RuCH-CH^{A}H^{B}$ moieties. These and the other ^{1}H and ^{13}C n.m.r. data imply unambiguously that there are two co-ordination position isomers. We tried to separate these by column chromatography, but in vain.

In the $^{13}C-\{^{1}H\}$ n.m.r. spectrum each of two ruthenium-bonded methine carbons and two metal-bonded carbonyl carbons showed comparatively small coupling constants (4.9—7.3 and 9.8 Hz, respectively). Four ester carbonyl carbons resonated as singlets without coupling to phosphorus. We deduce that the PPh_3 ligand is located at a *cis* position to the ruthenium-bonded methine carbon and carbonyl and the ester carbonyl oxygen. As the stereochemistry of the 1-carbon is retained in the reaction course from (2) to (6), as discussed before, the configuration at this carbon in complex (4) should be the same as that in (2). Accordingly, structures (E)—(H) are possible as the monomeric unit of (4) (Figure 4). Since a metal-bonded carbonyl group and a metal-bonded alkyl group show comparatively strong *trans* influences,[17] they have a tendency to avoid ligating *trans* to each other. Then, structures (G) and (H) can be ruled out. Structure (F) is unfavourable owing to steric interaction between the PPh_3 ligand and the free ester group. Accordingly, the monomer unit of (4) is assigned to structure (E).

Since the monomer unit of (4) is composed of only one component (E), the two isomers of (4) are caused by different bridging modes in this unit. There are three possible bridging modes for the dimeric forms of (4), as illustrated in Figure 5: (I) with C_i symmetry, (J) with C_2 symmetry with respect to an axis perpendicular to the Cl–Cl line, (K) with C_2 symmetry with

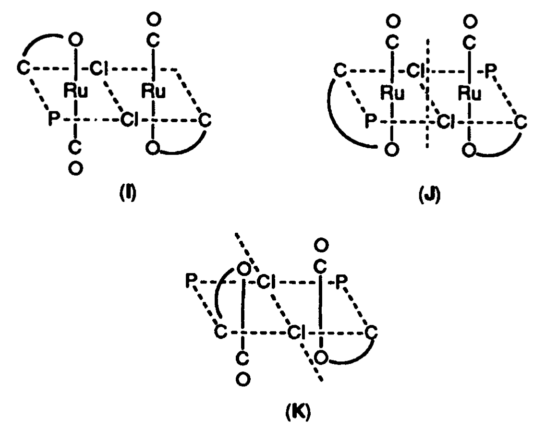


Figure 5. Possible bridging modes for the dimeric structures of complexes (4) and (5). C⁀O represents the 1,2-bis(alkoxycarbonyl)ethyl-C^1O chelate and P = PPh_3

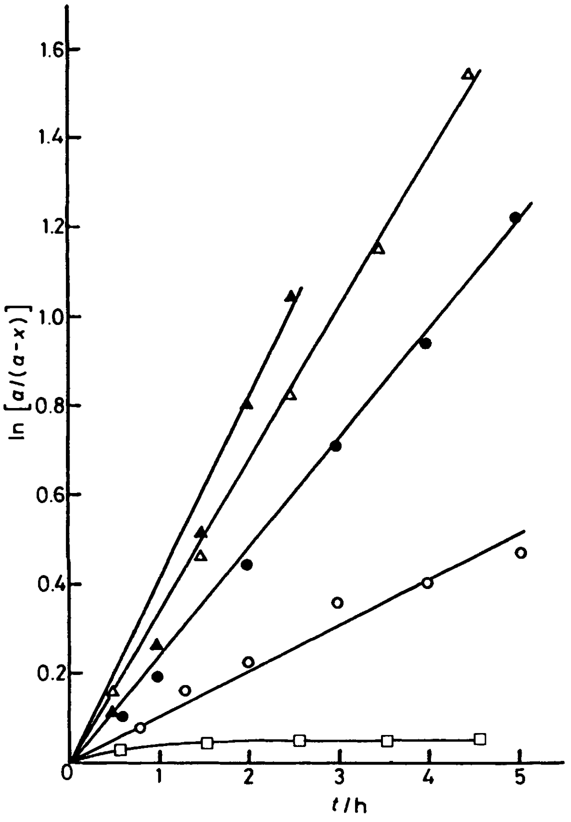


Figure 6. Plots of ln[$a/(a - x)$] *vs.* time for isomerization of dimethyl maleate catalyzed by PPh_3 or complex (1). Concentrations: PPh_3, 4.4×10^{-3} (□); (1), 1.7×10^{-3} (○), 2.8×10^{-3} (●), 4.4×10^{-3} (△), and 6.5×10^{-3} mol dm^{-3} (▲); a = 0.350 mol dm^{-3}

respect to an axis along Cl–Cl, and (L) with C_s symmetry. The $^{31}\text{P-}\{^1\text{H}\}$ n.m.r. spectrum of complex (4) showed two singlets at δ 61.95 and 62.87 p.p.m. The small chemical shift difference between these two singlets suggests that the chemical environments of the PPh_3 ligands in the two isomers are very similar to each other. Then, it seems that structure (K) is less favourable than (I) and (J), owing to the steric interaction among the two PPh_3 ligands and the bridging chlorides. Comparison of the structures of (2) and (4) indicates that dissociation of one PPh_3 ligand in (2) takes place at high temperature, followed by rearrangement of the chloro ligand and the co-ordinated ester group and by bridge formation with the chloro ligands of two neighbouring species to give (I) and (J) as the dimeric forms of (4).

When 2 mol of PPh_3 were added to a $CDCl_3$ solution of complex (4) at room temperature the regeneration of the mononuclear complex (2) was observed by $^{31}\text{P-}\{^1\text{H}\}$ n.m.r. spectroscopy.

Complex (5), the ethyl homologue of (4), showed almost analogous n.m.r. patterns to those of (4), indicating that (5) is composed of two isomers in a population ratio of about 55:45. In the ^{1}H n.m.r. spectrum of (5), the ester methylene protons appeared as about 50 signals, ascribed to 14 quartets, as shown in Table 1.

Catalytic Isomerization of Dimethyl Maleate.—During the course of the synthetic experiments on complex (4) it was found that (1), (2), and (4) catalyzed *cis-trans* isomerization of dimethyl maleate into dimethyl fumarate in a homogeneous solution of *m*-xylene, toluene, or dioxane above 100 °C. At 120 °C dimethyl maleate itself did not change at all. Moreover, PPh_3, which was to be liberated in the reaction from (1) to (2) or from (2) to (4) showed only a negligible degree of catalytic activity for the isomerization (Figure 6).

These findings prompted us to undertake kinetic studies of the isomerization in *m*-xylene at 120 °C. The correlation between the concentration of the initial dimethyl maleate (a), that of the dimethyl fumarate formed (x), and the reaction time (t) was analyzed. Plots of ln[$a/(a - x)$] *versus* t for several concentrations of the catalysts (1) and (4) were actually linear and passed through the origin (Figures 6 and 7), indicating that the reaction rate was proportional to the concentration of the remaining dimethyl maleate ($a - x$). Thus, the reaction rate follows equation (1), where k_1 is the first-order rate constant,

$$dx/dt = k_1(a - x) \qquad (1)$$

correlating only with the substrate. The rate constants, k_1, were proportional to the catalyst concentrations (c), as shown in Figure 8. Accordingly, the reaction rate follows equation (2), where k is a catalytic constant.

$$dx/dt = k_1(a - x) = kc(a - x) \qquad (2)$$

The catalytic constants, k, were 82, 52, and 38 dm^3 mol^{-1} h^{-1} for complexes (1), (2), and (4), respectively. The ratio of the catalytic constants per ruthenium atom is approximately 1.6:1.0:0.36 for (1), (2), and (4), respectively. Complex (1) involving three PPh_3 ligands was more active than (2) and (4), which contain two and one PPh_3 per ruthenium atom, respectively. Indeed, addition of PPh_3 to each of the catalysts accelerated the reaction rates (Figure 8).

Reactions of Complex (2) *with Diethyl Maleate.*—When complex (2) was treated with 15 times the molar ratio of diethyl maleate at 120 °C for 27 h the reaction mixture contained diethyl fumarate, but no diethyl maleate. Dimethyl fumarate was also detected in a fairly high yield on the basis of (2). After chromatographic separation, complex (5) was isolated in 33% yield. Treatment of (2) with five times the molar ratio of diethyl maleate at 120 °C afforded a mixture of (3), (4), (5), and diethyl and dimethyl fumarates. These components were characterized by comparison of the ^{1}H n.m.r. spectra with those of the respective authentic samples. These facts imply that complex (2) is also active for the catalytic isomerization of diethyl maleate. It is notable that the ethoxy derivatives (3) and (5) were formed from the reactions between the methoxy derivative (2) and diethyl maleate. These conversions correspond to the replacement of the unsaturated diester moiety overall and

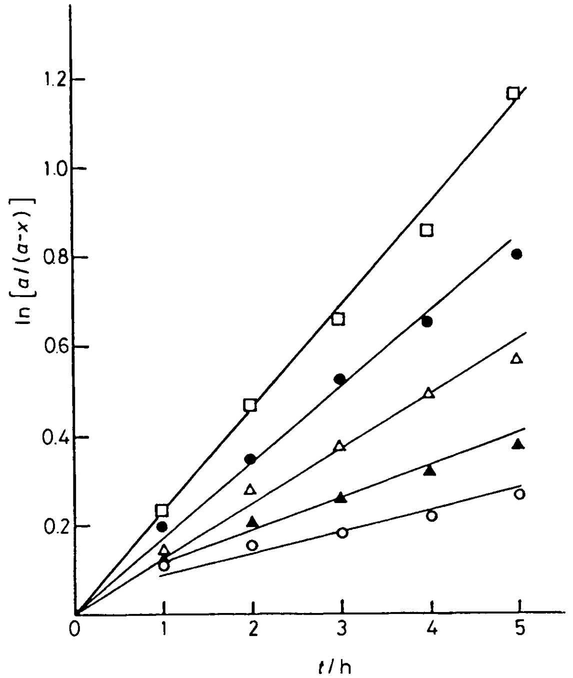


Figure 7. Plots of $\ln[a/(a-x)]$ *vs.* time for isomerization of dimethyl maleate catalyzed by complex (**4**). Catalyst concentration: 1.2×10^{-3} (○), 1.7×10^{-3} (▲), 2.8×10^{-3} (△), 4.3×10^{-3} (●), and 5.8×10^{-3} mol dm^{-3} (□); $a = 0.350$ mol dm^{-3}

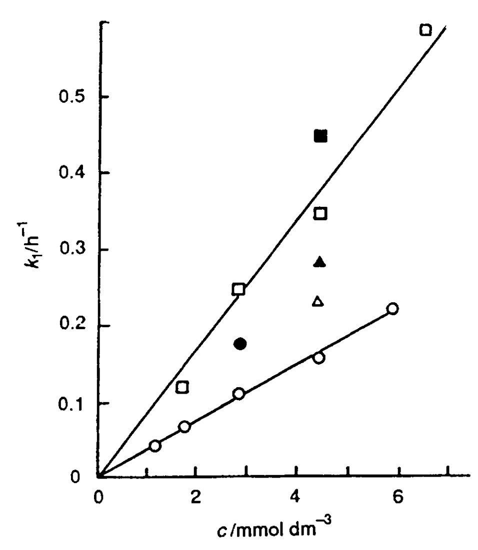


Figure 8. Correlation between the reaction rate (k_1) and the catalyst concentration (c). Catalyst: complex (**1**) (□), (**2**) (△), (**4**) (○), (**1**) + PPh_3 (1:1) (■), (**2**) + PPh_3 (1:1) (▲), and (**4**) + PPh_3 (1:1) (●)

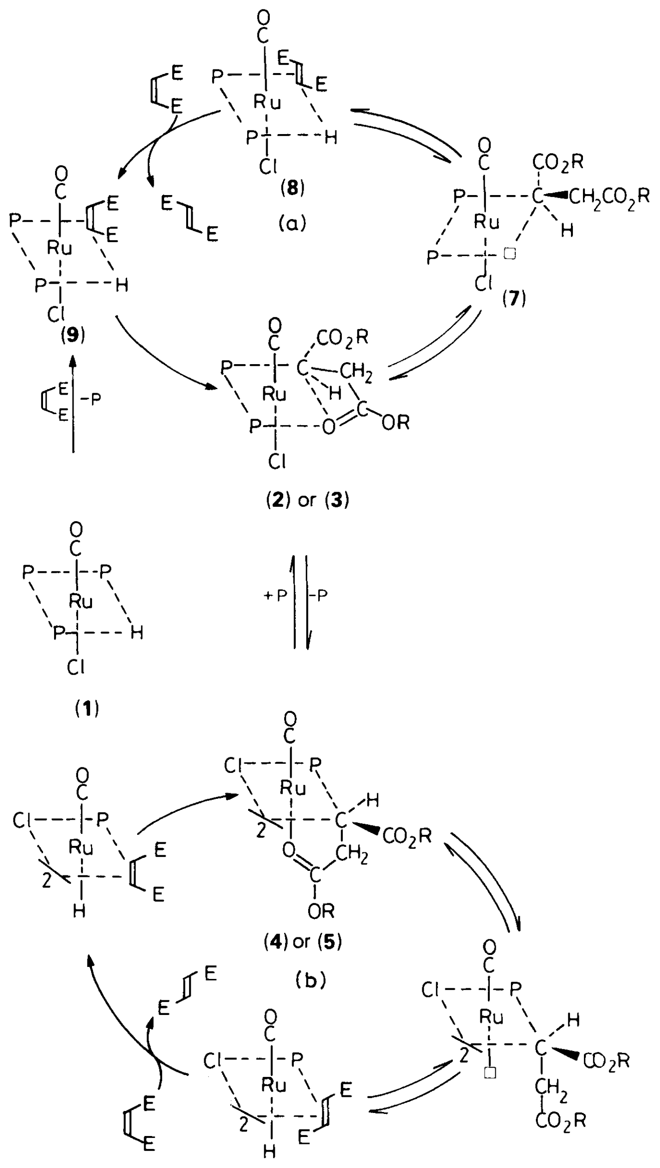


Figure 9. Possible mechanism for the isomerization of dialkyl maleate catalyzed by complexes (**1**), (**2**), and (**4**). P = PPh_3, E = CO_2R, and □ = a vacant site

indicate the participation of hydridoruthenium(II) species as transient intermediates.

Mechanism of the Catalytic Isomerization.—We have concentrated on the co-ordination of the ester group in complexes (**2**) or (**4**). Braunstein *et al.*[18] reported that an ester carbonyl group shows a weak *trans* influence and is co-ordinated weakly to a bivalent ruthenium centre in a chelating form; also that rapid exchange takes place between the co-ordinated and free ester groups.

Accordingly, it is reasonable that the C,O-chelating 1,2-bis(methoxycarbonyl)ethyl moiety in (**2**) becomes labile at high temperature and changes transiently to a unidentate ligand, leaving the oxygen-ligating site vacant (Figure 9). The resulting vacant site abstracts a β-hydrogen from the 1,2-bis(methoxycarbonyl)ethyl ligand (β elimination), and a hydrido(η^2-dimethyl fumarate)ruthenium(II) species (**8**) is formed. The predominant formation of the (η^2-dimethyl fumarate) species in this step is probably thermodynamic. The intermediate (**8**) substitutes easily the η^2-co-ordinated dimethyl fumarate for dimethyl maleate present in solution to yield the hydrido(η^2-dimethyl maleate)ruthenium(II) species (**9**), dissociating dimethyl fumarate. Consecutively, (**9a**) gives rise to the insertion reaction, regenerating (**2**). Thus, the catalytic cycle (a) of the isomerization is completed.

The case of the binuclear complex (**4**) is similar. However, the catalytic activity of (**4**) is much smaller than those of (**1**) and (**2**). This indicates that there is another catalytic cycle (b), in which the binuclear species act as the catalyst. Cycle (b) is clearly less active than (a). It is noteworthy that (**2**) and (**4**) not only initiate the catalytic isomerization, but also are reaction intermediates in the catalytic cycles.

Furthermore, the formation of (**3**) or (**5**) from (**2**) supports strongly the above-mentioned mechanism. When there is an excess of diethyl maleate in the solution, the η^2-co-ordinated dimethyl fumarate in (**8**) is replaced by diethyl maleate. The resulting hydrido(η^2-diethyl maleate) ruthenium(II) species (**9b**) gives rise to the insertion reaction to afford (**3**). Complex (**3**) loses one PPh_3 ligand and is converted into the binuclear species (**5**).

Effect of PPh_3.—Figure 8 shows unambiguously that the catalytic reaction rates increase with increasing quantities of PPh_3 in the reaction system. Considering the active cycle (a) and the less active one (b), the ratio of the two cycles depends on the molar ratio of PPh_3 to the total amount of the ruthenium(II) species and is kept constant during the reaction. It is not certain whether there is the third cycle which involves an ionic intermediate, derived from complex (**1**) by dissociation of the chloro ligand.

The difference between the activities of the catalytic cycles (a) and (b) is associated with the structures of the relatively stable intermediates, (**2**) and (**4**). In the case of the more active intermediate (**2**) the ester group is co-ordinated *trans* to PPh_3, which shows a comparatively strong *trans* influence.[17] On the other hand, the ester group in (**4**) is co-ordinated *trans* to the metal-bonded carbonyl group, which is expected to strengthen the co-ordination of the ester group to a degree by its π-accepting character and is reported to have a slightly weaker *trans* influence than that of PPh_3.[17] Accordingly, in (**2**) the ester co-ordination is more labile than in (**4**). This is the reason why (**2**) initiates the catalytic isomerization more easily than does (**4**).

In conclusion, this catalytic isomerization proceeds *via* an insertion–β-elimination mechanism, which is virtually the same as the mechanism proposed for the catalytic isomerization of alkenes.[1] We believe that the discussion in this paper gives a strong support to the latter mechanism.

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