

(Carboxylato)- and (α -Hydroxycarboxylato)-hydridotriphenylphosphine-ruthenium(II) Complexes and their Behaviour as Homogeneous Catalysts for Isomerisation and Hydrogenation of Alkenes

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Some new (carboxylato)hydrido(triphenylphosphine) derivatives of ruthenium have been prepared from $[\text{RuH}_2(\text{PPh}_3)_4]$ or $[\text{Ru}(\text{CO})\text{H}_2(\text{PPh}_3)_3]$ and dicarboxylic acids, $\text{HO}_2\text{C}(\text{CH}_2)_n\text{CO}_2\text{H}$ ($n = 1-4$), and α -hydroxy-acids. When $n = 2-4$, 2 : 1 (metal : dicarboxylate ligand) hydrido-complexes of formula $[\{\text{RuH}(\text{PPh}_3)_2\text{L}\}_2\{\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2\}]$ ($\text{L} = \text{PPh}_3$ or CO) are obtained. With malonic acid ($n = 1$) and α -hydroxy-acids 1 : 1 (metal : carboxylate group) complexes $[\text{RuH}(\text{O}_2\text{CCH}_2\text{CO}_2\text{H})(\text{PPh}_3)_3]$, $[\text{RuH}\{\text{O}_2\text{CCH}(\text{OH})\text{R}\}(\text{PPh}_3)_3]$ ($\text{R} = \text{H}$ or Ph), and $[\text{Ru}(\text{CO})\text{H}(\text{O}_2\text{CCH}_2\text{OH})(\text{PPh}_3)_2]$ are formed. The (carboxylato)hydrido-complexes are, in benzene solution, effective catalysts for the hydrogenation of alkenes and also for the isomerisation under an inert atmosphere. The activity and selectivity of the different complexes in the isomerisation and hydroisomerisation of pent-1-ene at 50 °C is reported and related to the steric and electronic factors of the carboxylate ligand. With optically active carboxylate ligands, such as (-)-R-phenylglycolate, a low asymmetric induction occurs in the hydrogenation and isomerisation of suitable alkenes.

THERE are few papers in the literature on the synthesis and catalytic activity of carboxylato-complexes of platinum metals with di-, poly-, or α -hydroxy-acids.¹⁻⁵ These are mainly compleximetric studies which were not

¹ P. T. Cheng, B. R. Loescher, and S. C. Nyburg, *Inorg. Chem.*, 1971, **10**, 1275.

² J. Chatt, F. G. Mann, and A. F. Wells, *J. Chem. Soc.*, 1938, 2087.

³ P. W. Van Leeuwen and A. Praat, *Rec. Trav. chim.*, 1970, **89**, 321.

directed to clarifying the structure and reactivity of the complexes obtained. On the other hand, many hydrido- and low oxidation-state mononuclear triphenylphosphine derivatives of ruthenium, rhodium, and iridium with monocarboxylate ligands have been described⁶ and

⁴ M. R. Churchill and R. Mason, *Nature*, 1964, **204**, 77.

⁵ M. J. Cleare and J. D. Moeschle, *Platinum Metals Rev.*, 1973, **17**, 2.

⁶ S. D. Robinson and M. F. Uttley, *J.C.S. Dalton*, 1973, 1912 and refs. therein.

used as alkene hydrogenation and isomerisation catalysts.⁷⁻⁹

We now report the synthesis of some new (carboxylato)hydridoruthenium(II) derivatives prepared from $[\text{RuH}_2(\text{PPh}_3)_4]$ or $[\text{Ru}(\text{CO})\text{H}_2(\text{PPh}_3)_3]$ and dicarboxylic and α -hydroxy-acids. These complexes of interest in catalysis in solution may also be regarded as suitable models for the corresponding complexes with linear macromolecular ligands, such as poly-acrylic and -methacrylic acids. These latter complexes, recently obtained^{10,11} from the same ruthenium starting complexes, have been used in experiments on heterogeneous catalysis of unsaturated substrates. The new results may therefore be used to gain information on the relation between homogeneous and heterogeneous catalysis. The ruthenium derivatives obtained have been used in the isomerisation and hydroisomerisation of pent-1-ene for studying the effect of the steric and electronic properties of different ligand groups^{12,13} on the reaction rate and isomeric composition. Furthermore, chiral complexes, simply prepared from optically active hydroxy-acids, can be used for asymmetric induction reactions.

RESULTS AND DISCUSSION

(Carboxylato)hydridotris(triphenylphosphine)ruthenium(II) Complexes.—The (carboxylato)hydridotris(triphenylphosphine) derivatives of Ru^{II} (Table I) were prepared

used as the reaction medium instead of primary alcohols⁶ to avoid the formation of carbonylated products arising from the decarbonylation of the alcohol.¹⁴

With dicarboxylic acids, $\text{HO}_2\text{C} \cdot [\text{CH}_2]_n \cdot \text{CO}_2\text{H}$ ($n = 2-4$), 2:1 (metal:dicarboxylate ligand) hydrido-complexes corresponding to the analytical formula $[\{\text{RuH}(\text{PPh}_3)_3\}_2\{\text{O}_2\text{C} \cdot (\text{CH}_2)_n \cdot \text{CO}_2\}]$ were obtained. Their infrared spectra contained a band in the range $1\ 970-1\ 963\ \text{cm}^{-1}$, attributable to the ruthenium-hydrogen stretching vibration, together with bands at $1\ 525\ \text{cm}^{-1}$ assignable to the asymmetric stretching of the carboxylate group and at $1\ 420-1\ 416\ \text{cm}^{-1}$ due to the symmetric stretching of the same group (Table I). The differences between the wavenumbers of the asymmetric and symmetric stretching frequencies of the carboxylate group are in the range $105-109\ \text{cm}^{-1}$, suggesting that this group functions as a bidentate ligand, in the solid state.⁶ The molecular weights in benzene (Mechrolab) (Table I) are about one third of the theoretical values, suggesting dissociation of one phosphine group per ruthenium.

In C_6D_6 or CDCl_3 solution, the ^1H n.m.r. spectra (Table I) all showed, beside resonances due to aliphatic and aromatic protons, a quartet (*ca.* τ 28) with central peaks having shoulders on their interior sides and quite similar to that recently reported by Hoffman and Caulton¹⁵ for $[\text{RuH}(\text{O}_2\text{CMe})(\text{PPh}_3)_3]$, indicating stereo-

TABLE I
Analytical and spectral data for the complexes

Complex	M.p. (θ°/cC)	Analysis (%) ^a				<i>M</i> ^c	I.r. data (cm^{-1}) (KBr)				^1H N.m.r. data (CDCl_3)	
		C	H	P	Ru ^b		$\nu(\text{RuH})$	$\nu(\text{CO})$	$\nu(\text{OCO})$ asym	$\nu(\text{OCO})$ sym	$\Delta\nu^f$	$\tau(\text{RuH})$ <i>J</i> (PH)
$[\{\text{RuH}(\text{PPh}_3)_3\}_2\{\text{O}_2\text{C} \cdot (\text{CH}_2)_2 \cdot \text{CO}_2\}]$	108-110	70.5 (71.05)	5.2 (5.1)	9.3 (9.8)	10.5 (10.65)	643 (1 894)	1 965m	1 524ms	1 418 (sh)	106	28.88 28.0 (q)	
$[\{\text{RuH}(\text{PPh}_3)_3\}_2\{\text{O}_2\text{C} \cdot (\text{CH}_2)_3 \cdot \text{CO}_2\}]$	101-102	70.7 (71.15)	5.4 (5.2)	9.2 (9.75)	10.2 (10.2)	627 (1 908)	1 970m	1 526ms	1 420 (sh)	105	28.74 28.1 (q)	
$[\{\text{RuH}(\text{PPh}_3)_3\}_2\{\text{O}_2\text{C} \cdot (\text{CH}_2)_4 \cdot \text{CO}_2\}]$	124-125	70.5 (71.4)	5.2 (5.25)	9.2 (9.65)	10.6 (10.5)	563 (1 922)	1 963m	1 525ms	1 416 (sh)	109	28.15 ^d 28.5 (q)	
$[\text{RuH}(\text{O}_2\text{CCH}_2\text{CO}_2\text{H})(\text{PPh}_3)_3]^e$	118-120	69.6 (69.0)	5.0 (5.0)	8.8 (9.35)	10.6 (10.2)	518 (992)	2 000m	1 537ms	1 450 (sh)	87	29.7 27.5 (q)	
$[\text{RuH}(\text{O}_2\text{CCH}_2\text{OH})(\text{PPh}_3)_3]$	122-124	69.0 (69.75)	5.2 (5.1)	9.4 (9.65)	11.0 (10.5)	451 (964)	2 015m	1 553ms	1 453 (sh)	100	28.94 ^d 27.6 (q)	
$[\text{RuH}(\text{O}_2\text{CCH}(\text{OH})\text{Ph})(\text{PPh}_3)_3]$	109-111	70.8 (71.6)	5.0 (5.15)	8.9 (8.95)	10.1 (9.7)	516 (1 040)	2 013m	1 555ms	1 450 (sh)	105	29.60 28.0 (q)	
$[\{\text{Ru}(\text{CO})\text{H}(\text{PPh}_3)_2\}_2\{\text{O}_2\text{C} \cdot (\text{CH}_2)_2 \cdot \text{CO}_2\}]$	220-222	65.5 (65.75)	4.7 (4.65)	8.3 (8.7)	14.4 (14.2)	653 (730)	2 040m	1 910s	1 520ms	1 449 (sh)	71	
$[\{\text{Ru}(\text{CO})\text{H}(\text{PPh}_3)_2\}_2\{\text{O}_2\text{C} \cdot (\text{CH}_2)_3 \cdot \text{CO}_2\}]$	136-138	65.9 (66.1)	5.1 (4.85)	8.3 (8.5)	14.1 (13.9)	653 (730)	2 060m	1 910s	1 520ms	1 450 (sh)	70	
$[\{\text{Ru}(\text{CO})\text{H}(\text{PPh}_3)_2\}_2\{\text{O}_2\text{CCH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2\}]$	186-187	63.7 (64.3)	4.8 (4.55)	8.8 (8.5)	14.4 (13.85)	653 (730)	2 020m	1 930s	1 540ms	1 445 (sh)	95	
$[\text{Ru}(\text{CO})\text{H}(\text{O}_2\text{CCH}_2\text{OH})(\text{PPh}_3)_2]$	149-150	64.2 (64.2)	4.5 (4.7)	8.6 (8.75)	13.9 (13.85)	653 (730)	2 034m	1 935s	1 549ms	1 460 (sh)	89	27.20 20.0 (t)
$[\text{Ru}(\text{CO})\text{H}(\text{O}_2\text{CCHMe}_2)(\text{PPh}_3)_2]$	172-175	66.0 (66.2)	5.0 (5.1)	8.2 (8.35)	13.9 (13.65)	653 (730)	1 983m	1 918s	1 510ms	1 458 (sh)	62	25.66 ^d 21.0 (t)

^a Calculated values are given in parentheses. ^b From X-ray fluorescence. ^c Mechrolab in C_6H_6 solution. ^d Solution in C_6D_6 . ^e $\nu(\text{CO})$ of free carboxylic group at $1\ 705\ \text{cm}^{-1}$. ^f $|\nu(\text{OCO})_{\text{asym}} - \nu(\text{OCO})_{\text{sym}}|$.

from $[\text{RuH}_2(\text{PPh}_3)_4]$ and the appropriate dicarboxylic or α -hydroxy-acid, according to a modification (especially of the solvent) of a method described by Robinson and Uttley⁶ for monocarboxylic acids. Isopropanol was

⁷ D. Rose, J. D. Gilbert, R. P. Richardson, and G. Wilkinson, *J. Chem. Soc. (A)*, 1969, 2610.

⁸ P. Legzdins, R. W. Mitchell, G. L. Rempel, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc. (A)*, 1970, 3322.

⁹ R. W. Mitchell, A. Spencer, and G. Wilkinson, *J.C.S. Dalton*, 1973, 846.

¹⁰ G. Braca, G. Sbrana, C. Carlini, and F. Ciardelli, in 'Catalysis Heterogeneous and Homogeneous', eds. B. Delmon and G. Jannes, Elsevier, Amsterdam, 1975, p. 307.

chemistry (I) with the hydrogen in a *cis* position with respect to three phosphorus atoms. The discrepancy between the ^1H n.m.r. data and the molecular-weight

¹¹ G. Braca, G. Sbrana, C. Carlini, and F. Ciardelli, in *Atti XII Congresso Nazionale di Chimica*, S. Margherita di Pula, 1975, C I 3, p. 325.

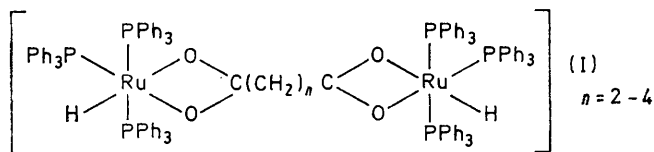
¹² D. Bingham, D. E. Webster, and P. B. Wells, *J.C.S. Dalton*, 1974, 1514 and refs. therein.

¹³ D. Bingham, D. E. Webster, and P. B. Wells, *J.C.S. Dalton*, 1974, 1519.

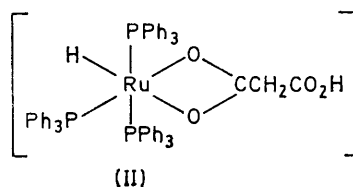
¹⁴ J. J. Levison and S. D. Robinson, *J. Chem. Soc. (A)*, 1970, 2947 and refs. therein.

¹⁵ P. R. Hoffman and K. G. Caulton, *J. Amer. Chem. Soc.*, 1975, 97, 4221.

measurements could be due to the presence of oxygen during the determination with the Mechrolab instrument; similar discrepancies have been reported for other ruthenium and rhodium complexes.^{6,7,16,17}



With malonic acid a 1:1 (metal:dicarboxylate ligand) complex of formula $[\text{RuH}(\text{O}_2\text{C}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})(\text{PPh}_3)_3]$ was obtained. The i.r. spectrum of this complex, beside the bands due to Ru-H and the bi-



dentate carboxylate group (asymmetric and symmetric) at 2000, 1537, and 1450 cm^{-1} respectively, showed a strong band at 1750 cm^{-1} attributable to CO stretching of the free carboxyl group. The above data, together with the ^1H n.m.r. spectrum, analogous to those of the complexes (I) (Table 1), are consistent with the stereochemistry (II). The formation of the 1:1 instead of a 2:1 species could depend on steric hindrance due to the closeness, in the malonic acid derivative, of the two carboxylate groups which does not allow co-ordination of two metallic units.

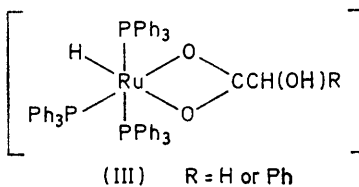
With α -hydroxy-acids, such as glycolic and (-)-R-phenylglycolic acids, complexes of formula $[\text{RuH}\{\text{O}_2\text{C}\cdot\text{CH}(\text{OH})\text{R}\}(\text{PPh}_3)_3]$ (R = H or Ph) were also obtained. The hydridic nature and the stereochemistry, (III), of these complexes is suggested by i.r. and ^1H n.m.r. data (Table 1). The hydroxyl group is not co-ordinated to the metal as indicated by the presence of the characteristic band of free OH at 3500 cm^{-1} ,¹⁸ and the carboxylate group is bidentate [$\nu(\text{OCO})_{\text{asym}}$ at 1555, $\nu(\text{OCO})_{\text{sym}}$ at 1455, and $\Delta\nu = 100 \text{ cm}^{-1}$].

Carbonyl(carboxylato)hydridobis(triphenylphosphine)-ruthenium(II) Complexes.—The carbonyl(carboxylato)hydridobis(triphenylphosphine) derivatives of Ru^{II} were prepared from $[\text{Ru}(\text{CO})\text{H}_2(\text{PPh}_3)_3]$ and the appropriate dicarboxylic or α -hydroxy-acid in boiling 2-methoxyethanol. A very pure ruthenium starting complex, prepared according to Ahmad *et al.*,¹⁹ is required.

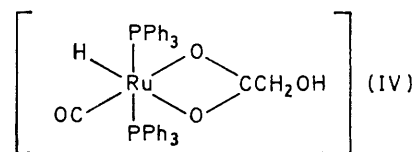
With glycolic acid a complex was obtained to which the stereochemistry (IV) is assigned as suggested by the presence in the i.r. spectrum of bands at 2034 and 1935 cm^{-1} , attributable to $\nu(\text{RuH})$ and $\nu(\text{CO})$ respectively, and by a symmetric triplet in the ^1H n.m.r. spectrum at τ 27.2 due to the hydrogen bound to ruthenium and

in a *cis* position with respect to two equivalent phosphorus atoms [$J(\text{PH})$ 20 Hz].⁶ Also in this case the carboxylate ligand is bidentate and the hydroxyl group is not co-ordinated (Table 1).

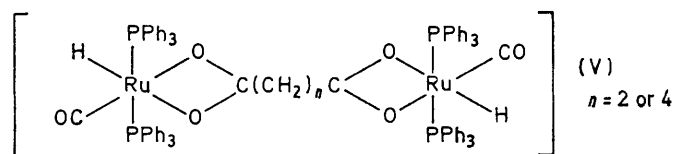
With succinic, adipic, and (-)-S-tartaric acids, complexes of formula $[\{\text{Ru}(\text{CO})\text{H}(\text{PPh}_3)_2\}_2\{\text{O}_2\text{C}\cdot(\text{CH}_2)_n\cdot\text{CO}_2\}]$ ($n = 2$ or 4) and $[\{\text{Ru}(\text{CO})\text{H}(\text{PPh}_3)_2\}_2\{\text{O}_2\text{C}\cdot(\text{CHOH})_2\cdot\text{CO}_2\}]$ were formed. Their i.r. spectra contained bands at 2020—2060 and 1910—1935 cm^{-1} , attributable, on intensity grounds, to $\nu(\text{RuH})$ and $\nu(\text{CO})$ respectively, together with bands indicative of bidentate carboxylate ligands (Table 1). No information on the stereochemistry of these complexes can be drawn from ^1H n.m.r. measurements owing to the insolubility of the



complexes in the common organic solvents; however, the i.r. data are essentially in agreement with those of the complex of glycolic acid and of other mono-



carboxylate complexes reported in the literature,⁶ and are compatible with stereochemistry (V).



Reactions catalysed by Ruthenium Carboxylate Complexes.—Isomerisation. The initial rate of reaction (50 °C) and the product composition, at different extents of isomerisation, of pent-1-ene catalysed by benzene solutions of the ruthenium complexes are given in Table 2. In the case of the 1:1 derivatives the activity decreased on decreasing the $\text{p}K_a$ of the acid as shown by the data in Table 2 for catalysts (1), (2), and (4). On the other hand, steric effects are also probably very important since substitution of a hydrogen atom in catalyst (3) with a phenyl group to give catalyst (2) caused a marked increase in activity, despite the fact that the $\text{p}K_a$ is approximately the same. Moreover, with the same carboxylate ligand, the activity decreased

¹⁶ D. R. Eaton and S. R. Stuart, *J. Amer. Chem. Soc.*, 1968, **90**, 4170.

¹⁷ K. G. Caulton, *J. Amer. Chem. Soc.*, 1974, **96**, 3005.

¹⁸ K. Nakamoto, P. J. McCarty, and B. Miniatus, *Spectrochim. Acta*, 1965, **21**, 379.

¹⁹ N. Ahmad, J. J. Levison, S. D. Robinson, and M. F. Uttley, *Inorg. Synth.*, 1974, **15**, 48.

markedly when a triphenylphosphine ligand was replaced by a carbonyl group [catalysts (1) and (5), and (3) and (6)].

This behaviour may be related to the mechanism

lytically active species formed from the original compound.

Path (ii), involving cleavage of one of the two Ru-O bonds of the carboxylate ligand by alkene, seems to be

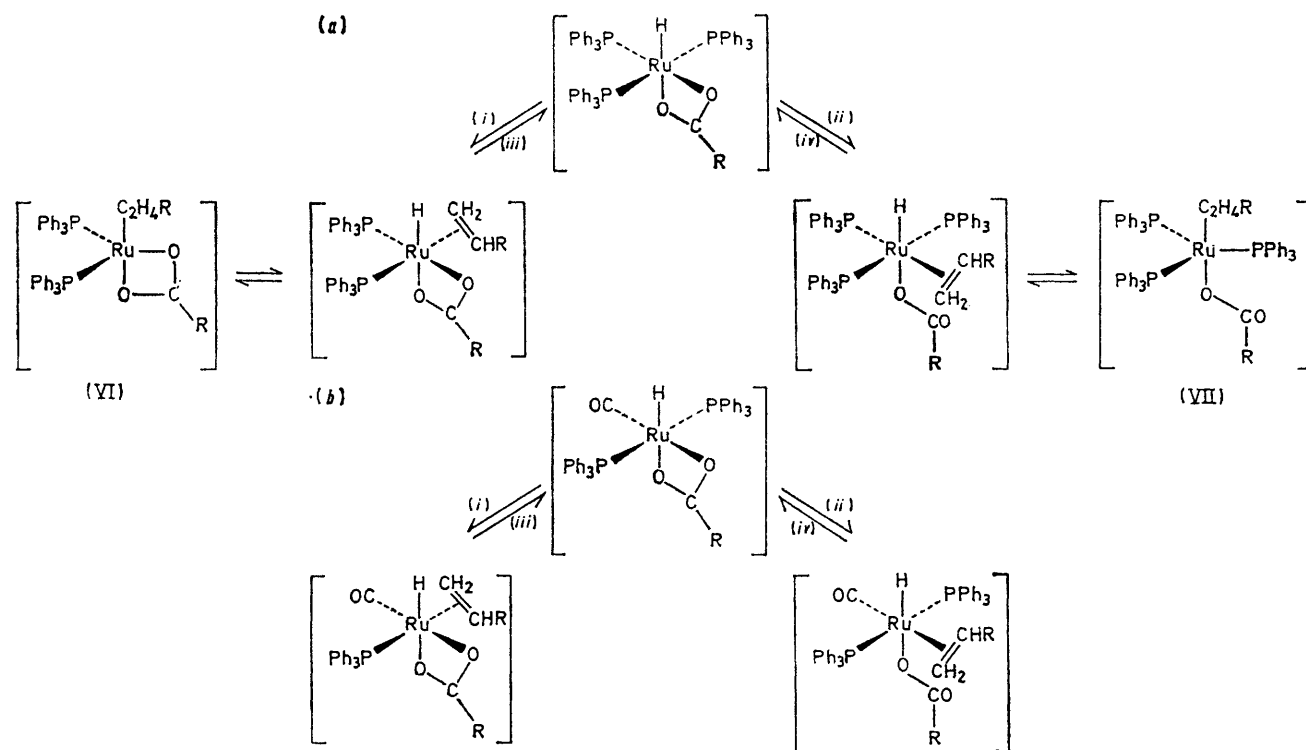
TABLE 2

Isomerisation of pent-1-ene under an inert atmosphere: [Catalyst] = 2.3×10^{-3} g-atom of Ru per litre; [pent-1-ene] = 0.83 mol dm^{-3} in benzene; 50°C

Catalyst	p <i>K</i> _a	Initial rate of reaction mmol ⁻¹ h ⁻¹	<i>cis</i> -Pent-2-ene to <i>trans</i> -Pent-2-ene ratio at conversion of	
			10%	70%
[RuH(O ₂ CCHMe ₂)(PPh ₃) ₃] (1)	4.84	10.1	1.9	1.2
[RuH{O ₂ CCH(OH)Ph}(PPh ₃) ₃] (2)	3.85	8.6	1.1	
[RuH(O ₂ CCH ₂ OH)(PPh ₃) ₃] (3)	3.83	4.3	1.6	1.2
[RuH(O ₂ CCH ₂ CO ₂ H)(PPh ₃) ₃] (4)	2.83	1.6	1.9	
[Ru(CO)H(O ₂ CCHMe ₂)(PPh ₃) ₂] (5)	4.84	4.1	0.45	0.35
[Ru(CO)H(O ₂ CCH ₂ OH)(PPh ₃) ₂] (6)	3.83	3.4	1.2	
[{RuH(PPh ₃) ₃] ₂ (O ₂ C·(CH ₂) ₂ ·CO ₂)] (7)	4.16	8.0	1.8	1.0
[{RuH(PPh ₃) ₃] ₂ (O ₂ C·(CH ₂) ₃ ·CO ₂)] (8)	4.34	5.5	1.8	1.1
[{RuH(PPh ₃) ₃] ₂ (O ₂ C·(CH ₂) ₄ ·CO ₂)] (9)	4.43	1.2	1.9	1.1
[{Ru(CO)H(PPh ₃) ₂] ₂ (O ₂ C·(CH ₂) ₂ ·CO ₂)] (10)	4.16	5.1	0.7	0.4

generally proposed for alkene isomerisation⁷ [Scheme (a)]. Electron-withdrawing R groups on the carboxylate ligand result in a lowering of the isomerisation rate due to a stronger bonding of triphenylphosphine to ruthenium

very likely and is in agreement with the loose co-ordination of this group as indicated by the X-ray crystal structure of the acetate derivative²² and by the easy replacement of this group by CO.⁷ In addition,



SCHEME (i) RCH=CH₂, -PPh₃; (ii) RCH=CH₂; (iii) PPh₃, -RCH=CH₂; (iv) -RCH=CH₂.

if the alkene co-ordination occurs through a displacement of a triphenylphosphine [path (i)], or to a stronger bonding of the carboxylate ligand in bidentate co-ordination if the path is (ii).^{20,21} This leads to the establishment of a lower concentration of the cata-

lytically active species. The i.r. spectrum of the catalyst recovered at the end of the reaction shows the presence of both hydridic and alkyl species with the carboxylate ligand bound in both unidentate [$\nu(\text{OCO})_{\text{asym}}$ at 1610 cm^{-1}] and bidentate form.

²⁰ W. R. May and M. M. Jones, *J. Inorg. Nuclear Chem.*, 1962, **24**, 511.

²¹ A. Yingst and D. H. McDaniel, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2922.

²² A. C. Skapski and F. A. Stephens, *J.C.S. Dalton*, 1974, 390.

The phosphine dissociation induced by alkene [path (*i*)], generally proposed in the isomerisation and hydrogenation mechanisms in the presence of tris(triphenylphosphine)ruthenium derivatives,^{7,9} cannot be excluded. In fact, the catalytic activity of these complexes in the alkene hydrogenation requires two vacant sites for oxidative addition of hydrogen, one arising from the dissociation of phosphine and the other from cleavage of the bidentate co-ordination of the carboxylate ligand.

carbonyl derivatives were mainly active for the isomerisation, and substrate hydrogenation in this case occurs only to a very small extent (Table 3). Simultaneously with hydrogenation, the isomerisation process took place at a higher rate than that observed under nitrogen (an increase by a factor of up to 30 was observed) as already reported for other ruthenium^{7,23} and rhodium complexes.²⁴

In the hydrogenation, in order for oxidative addition

TABLE 3

Hydroisomerisation of pent-1-ene: [Catalyst] = 2.3×10^{-3} g-atom of Ru per litre; [pent-1-ene] = 0.83 mol dm⁻³ in benzene; hydrogen pressure 1.06 atm; 50 °C

Catalyst	Initial rate of hydrogenation mmol l ⁻¹ h ⁻¹	Initial rate of isomerisation mmol l ⁻¹ h ⁻¹	<i>cis</i> -Pent-2-ene to <i>trans</i> -pent-2-ene ratio at conversion	
			low	high
[RuH(O ₂ CHMe ₂)(PPh ₃) ₃]	238	301	0.2	0.22
[RuH(O ₂ CCH ₂ OH)(PPh ₃) ₃]	176	224	1.4	0.8
[RuH(O ₂ CCH ₂ CO ₂ H)(PPh ₃) ₃]	113	21	2.04	1.6
[RuH{O ₂ CCH(OH)Ph}(PPh ₃) ₃]	77	42	1.4	1.2
[Ru(CO)H(O ₂ CCH ₂ OH)(PPh ₃) ₂]		36	1.2	0.9
[Ru(CO)H(O ₂ CCHMe ₂)(PPh ₃) ₂]		25	0.2	0.23
[[RuH(PPh ₃) ₃] ₂ {O ₂ C·(CH ₂) ₂ ·CO ₂ }]	232	332	0.27	0.18
[[RuH(PPh ₃) ₃] ₂ {O ₂ C·(CH ₂) ₂ ·CO ₂ }]	190	365	0.23	0.14
[[Ru(CO)H(PPh ₃) ₂] ₂ {O ₂ CCH(OH)CH(OH)CO ₂ }]	5	323	0.83	0.64
[[Ru(CO)H(PPh ₃) ₂] ₂ {O ₂ C·(CH ₂) ₂ ·CO ₂ }]	1.7	38	1.3	1.0

In the case of carbonyl(carboxylato)hydridobis(triphenylphosphine)ruthenium derivatives [Scheme (*b*)], it is likely that only path (*ii*) is operating, as the phosphine displacement is hindered when a π -acceptor carbonyl group is co-ordinated to the metal.

Concerning the isomeric distribution of internal olefins, preferential formation of *cis* olefin was observed as with other phosphine complexes of ruthenium, osmium, rhodium, and iridium.¹³ When a triphenylphosphine is replaced by a carbonyl group, the *trans* isomer predominated and this may be associated with less congestion of the ligands in the alkyl intermediate.¹²

In the case of the 2:1 (Ru:dicarboxylate ligand) complexes, the succinate [catalyst (7), Table 2] had the highest reaction rate and a decrease in activity occurred on passing to higher homologues, such as glutaric and adipic derivatives [catalysts (8) and (9)], in spite of rather similar pK_a values. This behaviour may be associated with steric effects as it is likely that, when the two metal moieties are very close, easier opening of the bidentate co-ordination occurs thereby leading to a higher concentration of the catalytically active species. This is confirmed by the failure to obtain the 2:1 (Ru:dicarboxylate ligand) complex in the case of malonic acid. Also in this case the same effect on the reaction rate and selectivity, as found for the 1:1 complexes, was observed when a triphenylphosphine was replaced by a carbonyl group [catalysts (7) and (10)].

Hydroisomerisation. The (carboxylato)hydrido(triphenylphosphine)ruthenium derivatives are also catalytically active at 50 °C and at atmospheric pressure for the hydrogenation of alkenes. On the other hand, the

of hydrogen to occur two free or weakly solvated co-ordination positions are necessary. According to the Scheme (*a*), from the alkylruthenium intermediate (VI) through cleavage of one Ru-O bond of the bidentate carboxylate ligand, or from the alkyl intermediate (VII) through displacement of a triphenylphosphine, intermediate square-planar complexes may be formed with two vacant sites available for hydrogen co-ordination. The positive effect of hydrogen on the isomerisation rate is related to the presence in solution of a catalytically active hydrido-species different from that present under nitrogen. The low activity of carbonyl derivatives for the hydrogenation may be due either to a lower tendency to phosphine dissociation or to the decreased basicity of the metallic centre, thus making the oxidative addition of hydrogen more difficult.

Concerning the isomeric distribution of internal olefins, the *cis:trans* ratios were generally lower than those found under nitrogen and decreased with olefin hydrogenation. This arises, as demonstrated by hydrogenating a 1:1 *cis:trans* pent-2-ene mixture under the same conditions in the presence of [[RuH(PPh₃)₃]₂{O₂C·(CH₂)₂·CO₂}], from the preferential hydrogenation of the *cis* isomer. (After 10 h, the *cis:trans* ratio was 0.29:1 with 23% conversion into pentane; no pent-1-ene was present.)

The hydrido(phenylglycolato)tris(triphenylphosphine)ruthenium complex prepared from (–)-*R*-phenylglycolic acid was tested as catalyst for asymmetric induction reactions. In the isomerisation of a racemic mixture of 4-methylhex-1-ene a very low stereoselective isomerisation occurred forming preferentially the *R*-internal

²³ P. S. Hallmann, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc. (A)*, 1968, 3143.

²⁴ W. Strohmeier and W. Rehder-Stirnweiss, *J. Organometallic Chem.*, 1971, **26**, C22.

olefin (optical purity, 0.7%). Also, in the hydrogenation of the prochiral 2-ethylhex-1-ene a low asymmetric induction was obtained (optical purity of (+)-S-3-methylheptane recovered, 0.4%).

EXPERIMENTAL

Starting triphenylphosphineruthenium complexes, $[\text{RuH}_2(\text{PPh}_3)_4]$ ¹⁴ and $[\text{Ru}(\text{CO})\text{H}_2(\text{PPh}_3)_3]$,¹⁹ were prepared as previously described. Dicarboxylic and α -hydroxyacids were used as purchased, reagent-grade degassed solvents were used throughout, and reactions and other operations were carried out under nitrogen. Alkenes (Fluka A.G.) were freed from peroxides by passage through a 30-cm column of activated alumina followed by fractional distillation from sodium-potassium alloy under nitrogen.

I.r. spectra were recorded on a Perkin-Elmer 225 spectrometer, ¹H n.m.r. spectra on a JEOL PS 100 instrument. M.p.s were measured in air on a Kofler hot-stage apparatus. Microanalyses were by Dr. Nuti, Facoltà di Farmacia, Pisa. Ruthenium was determined by X-ray fluorescence.²⁵ Molecular weights were measured on a Mechrolab apparatus.

Ruthenium Complexes.— μ -Succinato-bis[hydridotris(triphenylphosphine)ruthenium(II)], $[\{\text{RuH}(\text{PPh}_3)_3\}_2\{\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2\}]$. Succinic acid (0.118 g, 1.0 mmol) was added to a boiling suspension of dihydridotetrakis(triphenylphosphine)ruthenium (0.57 g, 0.5 mmol) in isopropanol (15 cm³). The mixture was heated under reflux for 30 min, during which time the solution cleared and a yellow solid commenced to precipitate. After cooling, methanol (20 cm³) was added and the precipitate was filtered off, washed with methanol, and dried *in vacuo* as yellow crystals (0.44 g, 93%).

The following complexes were similarly prepared: μ -glutarato-bis[hydridotris(triphenylphosphine)ruthenium(II)] as yellow crystals (75%); μ -adipato-bis[hydridotris(triphenylphosphine)ruthenium(II)] as yellow crystals (82%); hydrido(malonato)tris(triphenylphosphine)ruthenium(II) as yellow crystals (78%). Using a molar ratio of acid:ruthenium complex of 10:1, the following complexes were similarly prepared: (glycolato)hydridotris(triphenylphosphine)ruthenium(II) as yellow crystals (72%); hydrido[(-)-R-phenylglycolato]tris(triphenylphosphine)ruthenium(II) as yellow crystals (72%).

μ -Succinato-bis[carbonylhydridobis(triphenylphosphine)ruthenium(II)], $[\{\text{Ru}(\text{CO})\text{H}(\text{PPh}_3)_2\}_2\{\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2\}]$. Succinic acid (0.29 g, 2.5 mmol) dissolved in 2-methoxyethanol (7 cm³) was added to a boiling suspension of carbonyldihydridotris(triphenylphosphine)ruthenium (0.57 g, 0.62 mmol) in 2-methoxyethanol (7 cm³). The mixture was heated under reflux for 20 min, during which time a clear pale yellow solution was obtained. After cooling, methanol (30 cm³) was added resulting in the precipitation

of a white solid. The precipitate was filtered off, washed with methanol, and dried *in vacuo* (0.38 g, 84%).

The following complexes were similarly prepared: μ -adipato-bis[carbonylhydridobis(triphenylphosphine)ruthenium(II)] as a white product (71%); μ -(-)-S-tartrato-bis[carbonylhydridobis(triphenylphosphine)ruthenium(II)] as pale yellow crystals (43%).

Carbonyl(glycolato)hydridobis(triphenylphosphine)ruthenium(II), $[\text{Ru}(\text{CO})\text{H}(\text{O}_2\text{CCH}_2\text{OH})(\text{PPh}_3)_2]$. The product was prepared by the above method using ethanol as solvent (84%).

Carbonylhydrido(isobutyrate)bis(triphenylphosphine)ruthenium(II), $[\text{Ru}(\text{CO})\text{H}(\text{O}_2\text{CCHMe}_2)(\text{PPh}_3)_2]$. The product was obtained as pale yellow crystals (77%) according to the procedure described by Robinson and Uttley⁶ for the acetatohydrido-derivative.

Catalytic Reactions.—(a) *Isomerisation.* The kinetic experiments were carried out in a 50-cm³ thermostatted spherical reactor equipped with a magnetic stirrer and a short side arm closed with a serum cap. The catalytic solution was obtained by rapid mixing, under nitrogen, of benzene (25 cm³), ruthenium complex, and pent-1-ene (2.5 cm³). Small samples (10 μ l) were extracted through the serum cap at suitable intervals using a microlitre syringe and analysed by g.l.c., using columns packed with silver nitrate-benzyl cyanide on Chromosorb.

(b) *Hydroisomerisation.* The kinetic experiments were carried out using the reactor previously described, connected to a gas-volumetric apparatus containing hydrogen and maintained at a pressure of 1.06 ± 0.01 atm.*

(c) *Asymmetric isomerisation.* RS-4-Methylhex-1-ene (0.83 mol dm⁻³) in toluene was isomerised at 50 °C in the presence of hydrido[(-)-R-phenylglycolato]tris(triphenylphosphine)ruthenium (2.3×10^{-3} mol dm⁻³) up to 22% conversion. Under these conditions only a mixture of *cis*- and *trans*-R-4-methylhex-2-ene with an optical purity of 0.7% was obtained.

(d) *Asymmetric hydrogenation.* The prochiral olefin 2-ethylhex-1-ene (10 g) in benzene (10 cm³) was hydrogenated in an open glass vial contained in an autoclave under a hydrogen pressure of 50 atm in the presence of hydrido[(-)-R-phenylglycolato]tris(triphenylphosphine)ruthenium (0.12 g). After 50 h, >95% of the olefin had been hydrogenated to (+)-S-3-methylheptane with an optical purity of 0.4%.

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* 1 atm = 101 325 Pa.

²⁵ L. Leoni, G. Braca, G. Sbrana, and E. Giannetti, *Analyt. Chim. Acta*, 1975, **80**, 176.