Reactions of (η-Allyl)tricarbonylchlororuthenium(II) with Hydrogen and Unsaturated Substrates: Catalytic Hydrogenation and Isomerisation of Alkenes

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The complex [RuCl(C_3H_5)(CO)$_3$], (I), reacts with hydrogen to give polynuclear ' alkyloxycarbene derivatives arising from intramolecular carbonylation of the alkyl groups derived from hydrogenation and isomerisation of the allyl group. Reactions of (I) with unsaturated substrates such as acrylonitrile (acn), alkynes, butadiene, and acetylenic esters have been studied by i.r. and ^{1}H n.m.r. techniques. The solids [{RuCl(σ-C_3H_5)(CO)$_2$(acn)}$_2$], [{RuCl(OC·CR:CR'·C_3H_5)(CO)$_2$}$_2$] (R = R' = H; R = H, R' = Ph; and R = R' = Ph), and [RuCl{(C_4H_6)$_3$-C_3H_5}(CO)$_3$] have been isolated. In the case of diethyl acetylenedicarboxylate an alkenyl complex of formula [RuCl{C(CO_2Et):CH·C(OEt)O}(CO)$_3$] has been obtained. Under mild conditions complex (I) is shown to be an effective catalyst for homogeneous hydrogenation of terminal, internal, and cyclic alkenes, and carbonyl compounds. A very fast isomerisation of the substrate occurs during the hydrogenation; the isomerisation takes place also in the absence of hydrogen.

η-ALLYLRUTHENIUM complexes of formula [RuX(C_3H_5)(CO)$_3$] (X = Cl or Br) [1] have been shown to be catalysts for homogeneous oligomerisation and isomerisation of olefins.[2,3] The nature of the species obtained on reaction with olefins was studied in some detail.[2,3]

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[1] G. Sbrana, G. Braca, F. Piacenti and P. Pino, *J. Organometallic Chem.*, 1968, **13**, 240.

[2] G. Braca, G. Sbrana, and E. Benedetti, *Symp. Chem. Hydroformylation and Related Reactions*, Hungary, Veszprem, 1972, p. 127.

[3] G. Braca and G. Sbrana, *Chimica e Industria*, 1974, **56**, 110.

It was noted that, through a η–σ perturbation of the allyl group, co-ordinatively unsaturated species, reactive towards ligands capable of inserting into metal–carbon bonds, are formed and so catalytic cycles involving unsaturated substrates take place.[2,3] In order to obtain information on the mechanism of these catalytic reactions, the reactivity of (η-allyl)tricarbonylchlororuthenium(II), (I), towards hydrogen and unsaturated ligands, such as acrylonitrile (acn), butadiene, and acetylenic compounds, has been now examined. The catalytic activity of (I) for hydrogenations and isomerisations has also been investigated.

RESULTS

Reactions.—With hydrogen. (η-Allyl)tricarbonylchlororuthenium, (I), reacted in hydrocarbon solution with hydrogen under mild conditions (40—50 °C, 1—15 atm).* When the reaction was carried out in benzene *in a closed system* (1—10 atm of hydrogen at 50 °C), a dark yellow solution was obtained from which a yellow solid, (II), could be precipitated by adding n-pentane [ν(CO) at 2 130w, 2 060s, and 1 998s cm^{-1} (KBr)]. When the reaction was carried out at atmospheric pressure *ca.* 1 mol of hydrogen per mol of (I) was consumed. Solid (II) consists of a mixture of two polynuclear isomeric compounds containing the $\mathrm{MeCH_2CH_2CO}$ and $\mathrm{Me_2CHCO}$ groups respectively bridging two ruthenium atoms in a ' carbene ' arrangement [ν(CO) (carbene) at 1 540s cm^{-1}],[4] as indicated by the presence of all the characteristic i.r. and/or ^{1}H n.m.r. absorptions due to n-propyl and isopropyl groups, and terminal and bridging chlorine atoms [ν(Ru–Cl) at 323w, 278w, and 269w cm^{-1}].[5] Other evidence supporting the existence of the ' carbene ' groups is provided by (*i*) the formation of a mixture of methyl n-butyrate and methyl isobutyrate by reaction of (II) with a methanolic iodine solution or with CO and methanol (150 °C, 150 atm), and (*ii*) the presence in the mass spectrum, besides a fragment at *m/e* 263 corresponding to the ion $[\mathrm{RuCl(OCC_3H_7)(CO)_2}]^+$, of ions arising from fragmentation of the $\mathrm{C_3H_7CO}$ groups.

Treatment of a benzene solution of (II) with triphenylphosphine at 60 °C caused the polynuclear structure to break and release carbon monoxide with the formation of a monomeric crystalline product of formula $[\mathrm{RuCl(OCC_3H_7)CO(PPh_3)_2}]\cdot\mathrm{C_6H_6}$ showing in its i.r. spectrum a strong absorption at 1 638 cm^{-1} assignable to a σ-bonded acyl group.[3] The presence of more than one absorption band in the terminal-carbonyl-stretching region is probably due to formation of different geometric isomers of a presumably five-co-ordinate structure with lattice benzene.

When hydrogen was ***bubbled*** at atmospheric pressure through a hydrocarbon solution of (I) at 40—50 °C a dark red solid was precipitated. This intensely coloured product may be formulated as $[\{\mathrm{RuCl(CO)_3}\}_2]$, (III) [$\nu$(CO) at 2 033s, 2 000s, and 1 965s cm^{-1}], with probably a Ru–Ru bond like the analogous complexes $[\{\mathrm{RuCl(CO)_2PR_3}\}_2]$.[6] Complex (III) was not obtained pure, being contaminated with small quantities of (II), not easily removable.

With triphenylphosphine. The η-allylruthenium complexes reacted with triphenylphosphine releasing 1 mol of carbon monoxide. In the case of $[\mathrm{RuBr(C_3H_5)(CO)_3}]$, the complex $[\mathrm{RuBr(C_3H_5)(CO)_2PPh_3}]$, (IV), was isolated and characterised.

With nitriles. Propiononitrile did not react with (I) under a variety of reaction conditions. On the other hand, treatment of (I) in toluene solution with acrylonitrile (acn) (70 °C) caused evolution of 1 mol of carbon monoxide and formation of an air-stable complex $[\{\mathrm{RuCl(C_3H_5)(acn)(CO)_2}\}_2]$, (V), insoluble in the common organic solvents. Suggestions about the structure of this complex are essentially based on i.r. spectra. Bonding of the acn ligand through its olefinic carbon–carbon bond is suggested by the following evidence: (*i*) the CN stretching frequency (2 240 cm^{-1}) is essentially unchanged with respect to the free ligand (2 235 cm^{-1});[7,8] (*ii*) the disappearance of the high-intensity absorptions at 1 608 [ν(C:C)] and at 967 cm^{-1} [$\delta(\mathrm{CH_2})$] of the free ligand; and (*iii*) the low decrease in ν(CO) (12—20 cm^{-1}) relative to (I).[7]

In the solid state the complex probably is dimeric. In fact no terminal Ru–Cl bands were observed in the i.r. spectrum of (V) near 330 cm^{-1}, but bands at 260—280 cm^{-1} were present corresponding to stretching modes of bridging chlorine atoms.[5] The allyl group is σ-bonded to the metal as indicated by the presence of all the i.r. absorptions due to an unco-ordinated vinyl group [ν(C:C) at 1 640, $\delta(\mathrm{CH_2})$ (in plane) at 1 415, and $\gamma(\mathrm{CH_2})$ (out-of-plane) at 990 and 915 cm^{-1}]. The stretching frequency of the carbon–carbon double bond of the co-ordinated acn could be recognised in the low-intensity band at 1 495 cm^{-1} or in the broad one at 1 420—1 460 cm^{-1} containing also the bending absorptions of the $\mathrm{CH_2}$ groups. The presence of two bands in the carbonyl-stretching region (2 058 and 1 982 cm^{-1}) suggests a *cis*-position for the CO groups.

Treatment of (V) with triphenylphosphine caused cleavage of the halogen bridge with formation of the monomeric complex $[\mathrm{RuCl(\sigma\text{-}C_3H_5)(CO)_2(acn)PPh_3}]$, (VI). Its i.r. spectrum (Table 1) showed, besides the same set of bands present in the spectrum of (V) assigned to acn complexed through the double bond and to the σ-bonded allyl group, an absorption at 320 cm^{-1} attributed to terminal Ru–Cl stretching vibration. ^{1}H N.m.r. spectra do not provide further information on the structure of (V) and (VI) due to the limited solubility of these complexes.

With alkynes and butadiene. Alkynes (acetylene, phenylacetylene, and diphenylacetylene) reacted at 60—90 °C in aromatic hydrocarbons with (I) to give acyl complexes of formula $[\{\mathrm{RuCl(OCCR{:}CR'C_3H_5)(CO)_2}\}_2]$ [(VII) R = R′ = H; (VIIIa) R = H, R′ = Ph; (VIIIb) R = Ph, R′ = H; and (IX) R = R′ = Ph] arising from insertion of alkyne and CO into an allyl–ruthenium bond. Evidence of the presence in the complexes of the $\mathrm{C_3H_5\text{-}CR'{:}CRCO}$ group is provided by (*i*) the formation of α,β-unsaturated aldehydes by reaction of (VII), (VIIIa), and (VIIIb) with HCl, (*ii*) the formation, in the reaction of (VII) with carbon monoxide and methanol, of methyl n-hexanoate by alcoholysis of the unsaturated acyl group and hydrogenation of this by transfer of hydrogen from alcohol, and (*iii*) the presence in the mass spectra of the complexes of peaks at *m/e* 95, 171, and 247 for (VII),

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* 1 atm = 101 325 Pa.

[4] G. Braca, G. Sbrana, and G. Scandiffio, *Chimica e Industria*, 1974, **56**, 570.

[5] E. Benedetti, G. Braca, G. Sbrana, F. Salvetti, and B. Grassi, *J. Organometallic Chem.*, 1972, **37**, 361.

[6] D. F. Gill, B. E. Mann, and B. L. Shaw, *J.C.S. Dalton*, 1973, 311.

[7] L. M. Ziegler and R. K. Sheline, *Inorg. Chem.*, 1965, **4**, 1230.

[8] B. L. Ross, J. G. Grasselli, W. M. Ritchey, and H. D. Kaesz, *Inorg. Chem.*, 1963, **2**, 1023.

(VIIIa) or (VIIIb), and (IX) respectively, corresponding to $[C_3H_5CR'{:}CRCO]^+$ fragments. I.r. spectra (Table 1) showed absorptions at 1 610—1 635 cm^{-1}, assignable to the CO stretching frequency of an acyl group,[9] and all the characteristic vibrational modes of a vinyl group and of conjugated internal double bonds.[10] The presence of bands near 280 cm^{-1}, assignable to Ru–Cl stretching with bridging chlorine atoms,[5] suggests a dimeric structure in the solid state for these complexes. In donor solvents, such as methyl ethyl ketone, the complexes exist probably in a monomeric form as indicated by the molecular weight (Mechrolab osmometer).

TABLE 1

I.r. and u.v. data for the complexes

Complex	I.r. data (cm^{-1}) (KBr)							U.v. data (MeOH)	
	ν(CN)	ν(CO)	ν(CO) ester	ν(CO) acyl	$\nu(C{:}CH_2)$	$\nu(C{:}C)$	ν(Ru–Cl)	$\lambda_{max.}$ nm	ε l mol^{-1} cm^{-1}
$[RuBr(C_3H_5)(CO)_2PPh_3]$ (IV)		2 042s 1 975s				1 476m [a]	[b]		
$[\{RuCl(\sigma\text{-}C_3H_5)(CO)_2(acn)\}_2]$ (V)	2 240s	2 048vs 1 982vs			1 640m 1 495w [d]		280m [c] 260m [c]		
$[RuCl(\sigma\text{-}C_3H_5)(CO)_2(acn)PPh_3]$ (VI)	2 225s	2 040vs 1 975vs			1 640m 1 481m [d]		320w [e]		
$[\{RuCl(OC{\cdot}CH{:}CH{\cdot}C_3H_5)(CO)_2\}_2]$ (VII)		2 048vs 1 980vs		1 635vs	1 655s	1 565m	280m [c]	222 265	11 500 5 900
$[\{RuCl(OC{\cdot}CH{:}CPh{\cdot}C_3H_5)(CO)_2\}_2]$ (VIIIa)		2 030vs		1 618vs	1 640 (sh)	1 570s	280m [c]	198 232 275	48 600 23 300 5 960
$[\{RuCl(OC{\cdot}CPh{:}CH{\cdot}C_3H_5)(CO)_2\}_2]$ (VIIIb)		1 955vs							
$[\{RuCl(OC{\cdot}CPh{:}CPh{\cdot}C_3H_5)(CO)_2\}_2]$ (IX)		2 030vs 1 951vs		1 610vs	1 635 (sh)	1 560s	270m [c]		
$[RuCl\{(C_4H_6)_3C_3H_5\}(CO)_3]$ (X)		2 120m 2 055vs 1 988vs			1 635w		320m [e]		
$[RuCl\{C(CO_2Et){:}CH{\cdot}C(OEt)O\}(CO)_3]$ (XI)		2 140m 2 060vs 1 990vs	1 708s [f] 1 590s [g]			1 625m	325w [e]		
$[\{RuCl[OC{\cdot}CH{:}C(CO_2Et){\cdot}C_3H_5](CO)_2\}_2]$ (XIIa)		2 050vs	1 715s [f]	1 635s	1 660m	1 590m	280w [c]		
$[\{RuCl[OC{\cdot}C(CO_2Et){:}CH{\cdot}C_3H_5](CO)_2\}_2]$ (XIIb)		1 970vs							

[a] $\nu(C\text{:-:}C\text{:-:}C)_{asym}$ of η-allyl group. [b] ν(Ru–Br) at 230w cm^{-1}. [c] Bridging. [d] Stretching frequency of C:C of co-ordinated acn. [e] Terminal. [f] Free ester. [g] Co-ordinated ester.

TABLE 2

^1H N.m.r. data (τ) for complexes obtained in the reaction of $[RuCl(C_3H_5)(CO)_3]$ with acetylenic compounds [a]

Complex	Assignments			Description
	=CH	C_3H_5	C_2H_5	
(VII)	1·8 (m) (1) 3·2 (m) (1)	6·5—8·6 (m) (5)		Complex multiplets Very broad
(XI)	7·2 (m) (1) [b]		5·7 (q) (4) 8·8 (t) (6)	Multiplet very broad
(XIIa) and (XIIb)	4·2 (m) (1)	6·2—8·0 (m) (5)	5·8 (q) (2) 8·7 (t) (3)	Multiplets very broad

[a] Except where stated, spectra were recorded at 60 mHz on solutions in $CDCl_3$ with $SiMe_4$ as internal reference. Numbers in parentheses indicate relative intensities of peaks. [b] Solution in CD_3COCD_3.

^1H N.m.r. data (Table 2) confirm the presence in the complexes of the $C_3H_5CR'{:}CRCO$ group: the spectrum of (VII) showed two multiplets at τ 1·8 and 3·2, assignable to the two protons of the acetylene inserted between the CO and the allyl group.[11-13] The spectrum of the product obtained on reaction of (I) with phenylacetylene was very complex and does not allow [11,12] a sure distinction to be drawn between the two possible structures, namely $RuCl(OC{\cdot}CH{:}CPh{\cdot}CH_2{\cdot}CH{:}CH_2)$ (VIIIa) and $RuCl(OC{\cdot}CPh{:}CH{\cdot}CH_2{\cdot}CH{:}CH_2)$ (VIIIb). However, the distorted quartet at τ 1·8 (J 2 Hz) may be assigned to the proton H(2) long-range coupled with H(4) protons of isomer (VIIIa), and the complexity of the spectrum in the region between τ 1·9 and 2·8 does not exclude the presence of resonances of H(3) proton in isomer (VIIIb); the multiline broad resonance observed between τ 6·2 and 8·5 is attributed to the allyl group, the broadening being explained by an intra- or inter-molecular interaction between the vinyl group and the ruthenium atom.[14,15]

U.v. spectra (Table 2) showed, besides very intense absorptions at 198—232 nm attributable to an electronic transition of the conjugated acyl ligand, an absorption at 265—275 nm assignable to a charge-transfer metal–

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[9] G. Booth and J. Chatt, *J. Chem. Soc.* (*A*), 1966, 634.

[10] T. G. Appleton, H. C. Clark, R. C. Poller, and R. J. Puddephatt, *J. Organometallic Chem.*, 1972, **39**, C13.

[11] B. L. Booth and R. G. Hargreaves, *J. Chem. Soc.* (*A*), 1969, 2766.

[12] B. L. Booth and R. G. Hargreaves, *J. Chem. Soc.* (*A*), 1970, 308.

[13] A. Nesmeyanov, M. Rubinskaya, L. Rybin, and V. Kaganovich, *J. Organometallic Chem.*, 1971, **31**, 257.

[14] Y. Takahashi, S. Sakai, and Y. Ishii, *J. Organometallic Chem.*, 1969, **16**, 177.

[15] A. Greco, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 3476.

ligand band.[16] The closeness of the spectra of (VII) and (VIIIa) and (VIIIb) in this region may mean that the terminal double bond is involved in the charge transfer rather than the internal one.

An analogous insertion reaction into the allyl–ruthenium bond occurred when (I) was treated with butadiene at 70—80 °C in hydrocarbon solution. A product arising from addition of three molecules of butadiene to (I), corresponding to an empirical formula $[RuCl(C_{12}H_{18}C_3H_5)(CO)_3]$, (X), was separated and identified. Its i.r. spectrum showed absorption bands assignable to a terminal vinyl group (1 635, 990, and 910 cm^{-1}) and to a *trans*-carbon–carbon double bond (962 cm^{-1}). The ^1H n.m.r. spectrum of (X) consisted of two patterns of resonances, not resolved in their fine structure, at τ 9·2—7·2 (aliphatic protons) and 5·4—3·3 (olefinic protons). The intensity ratio of these two groups of protons (15 : 8) is in agreement with a structure arising from insertion of three molecules of butadiene into an allyl–ruthenium bond, the last of which being π-bonded to the metal.[14, 17-19]

With acetylenic esters. Diethyl acetylenedicarboxylate reacted with (I) under the same conditions specified above for the alkynes to give an alkenyl complex corresponding to the formula $[RuCl\{C(CO_2Et)\dot{:}CH{\cdot}C(OEt)O\}(CO)_3]$, (XI), arising from insertion of the acetylenic ligand into a ruthenium–hydrogen bond, probably resulting in loss of allene (see Scheme 1). Evidence for the formation of (XI) is provided by (*i*) the parent peak and peaks corresponding to successive loss of three carbon monoxide molecules in the mass spectrum with a fragmentation analogous to that observed for other alkenyl complexes,[11] (*ii*) three bands in the i.r. spectrum assignable to terminal $\nu(CO)$ (Table 1) and a band assignable to internal $\nu(C\dot{:}C)$ at 1 625 cm^{-1}, (*iii*) the absence of any absorption attributable to acyl and allyl groups, and (*iv*) the presence in the ^1H n.m.r. spectrum of only one olefinic proton at τ 7·2.[13] The terminal Ru–Cl stretching frequency at 325 cm^{-1} and the two strong absorptions at 1 708 and 1 590 cm^{-1}, assignable respectively to $\nu(CO)$ of free and co-ordinated ester groups,[11, 12] suggest for (XI) in the solid state the molecular arrangement reported in Scheme 1, analogous to that proposed for $[Mn\{C(CO_2Me)\dot{:}CH{\cdot}C(OMe)O\}(CO)_4]$ [11] and $[Ru\{C(CO_2Me)\dot{:}CH{\cdot}C(OMe)O\}(PPh_3)_2(cp)]$ (cp = η-cyclopentadienyl).[20]

Ethyl propiolate formed a mixture both of the alkenyl and acyl derivatives. The less soluble acyl derivative was separated in a pure state. Although the i.r. and ^1H n.m.r. spectra (Tables 1 and 2) and analytical data support the acyl structure, they do not allow a distinction to be drawn between the two possible structures, namely $[RuCl\{OC{\cdot}CH\dot{:}C(CO_2Et){\cdot}C_3H_5\}(CO)_2]$, (XIIa), and $[RuCl\{OC{\cdot}C(CO_2Et)\dot{:}CH{\cdot}C_3H_5\}(CO)_2]$, (XIIb). The more soluble component of the reaction mixture is suggested to be the alkenyl derivative by spectroscopic evidence (i.r. and ^1H n.m.r.).

Hydrogenation and Isomerisation of Alkenes.—Complex (I) is an effective catalyst for the hydrogenation of terminal, internal, and cyclic alkenes at a temperature of 80—100 °C under a hydrogen pressure in the range 1—20 atm (Table 3). Very fast isomerisation of the substrate occurs during the hydrogenation; isomerisation takes place also in the absence of hydrogen.[2, 3] Terminal alkenes are hydrogenated faster than cyclic and internal ones, thus contrasting with ruthenium phosphine systems [21-23] which are reported to be ineffective in hydrogenation of internal alkenes.

TABLE 3

Hydrogenation and isomerisation of alkenes by $[RuCl(C_3H_5)(CO)_3]$: [Catalyst] = 7·16mM in toluene; [Alkene] = 4·15M; hydrogen pressure 20 atm; 100 °C

Alkene	Reaction time/h	Hydrogenation/ %	Isomerisation/ %
Propene	4	82·0	
But-1-ene [a]	2	22·4	67·0
Hex-1-ene	4	41·2	47·3
cis- + *trans*- Hex-2-ene	4	8·9	3·3 [b]
Cyclohexene	4	37·8	
But-1-ene [a, c]	2		54·7

[a] [Catalyst] = 6·12mM. [b] To hex-1-ene. [c] In the absence of hydrogen.

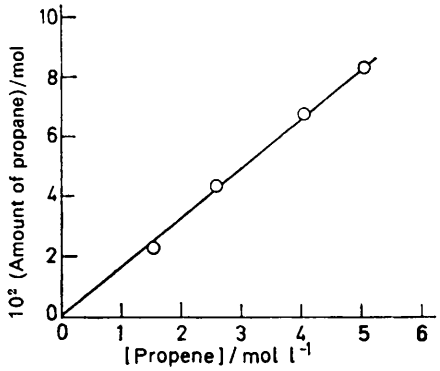

FIGURE 1 Plot of the amount of propane formed after 4 h hydrogenation of propene against olefin concentration in the presence of 7·16mM-$[RuCl(C_3H_5)(CO)_3]$ at 100 °C and 20 atm hydrogen in toluene

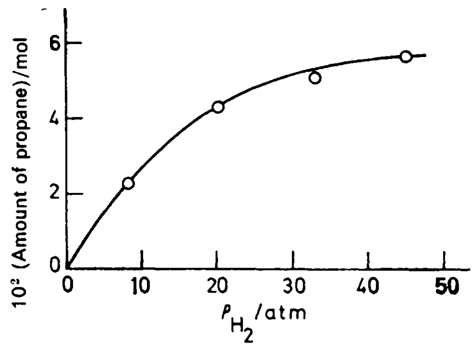

FIGURE 2 Plot of the amount of propane formed after 4 h hydrogenation of propene against hydrogen pressure in the presence of 7·16mM-$[RuCl(C_3H_5)(CO)_3]$ and 2·65M-propene in toluene at 100 °C

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[16] R. E. Clark and P. C. Ford, *Inorg. Chem.*, 1970, **9**, 227.

[17] R. P. Hughes and J. Powell, *J. Amer. Chem. Soc.*, 1972, **94**, 7723.

[18] G. Wilke, B. Bogdanovich, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter, and H, Zimmermann, *Angew. Chem. Internat. Edn.*, 1966, **5**, 151.

[19] J. P. Durand, F. Dawans, and P. M. Teyssie, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1970, **8**, 979.

[20] T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 106.

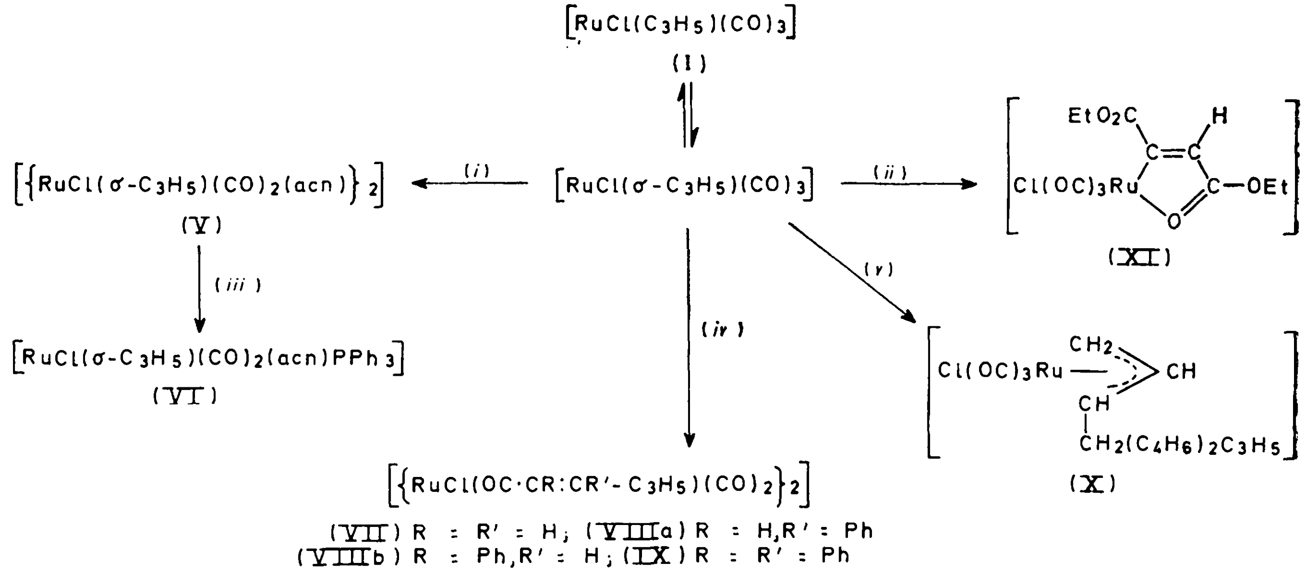
[21] P. S. Hallmann, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 3143.

[22] B. Hui and B. R. James in *Proc. 4th Internat. Conf. Organometallic Chem.*, Bristol, 1969, L6.

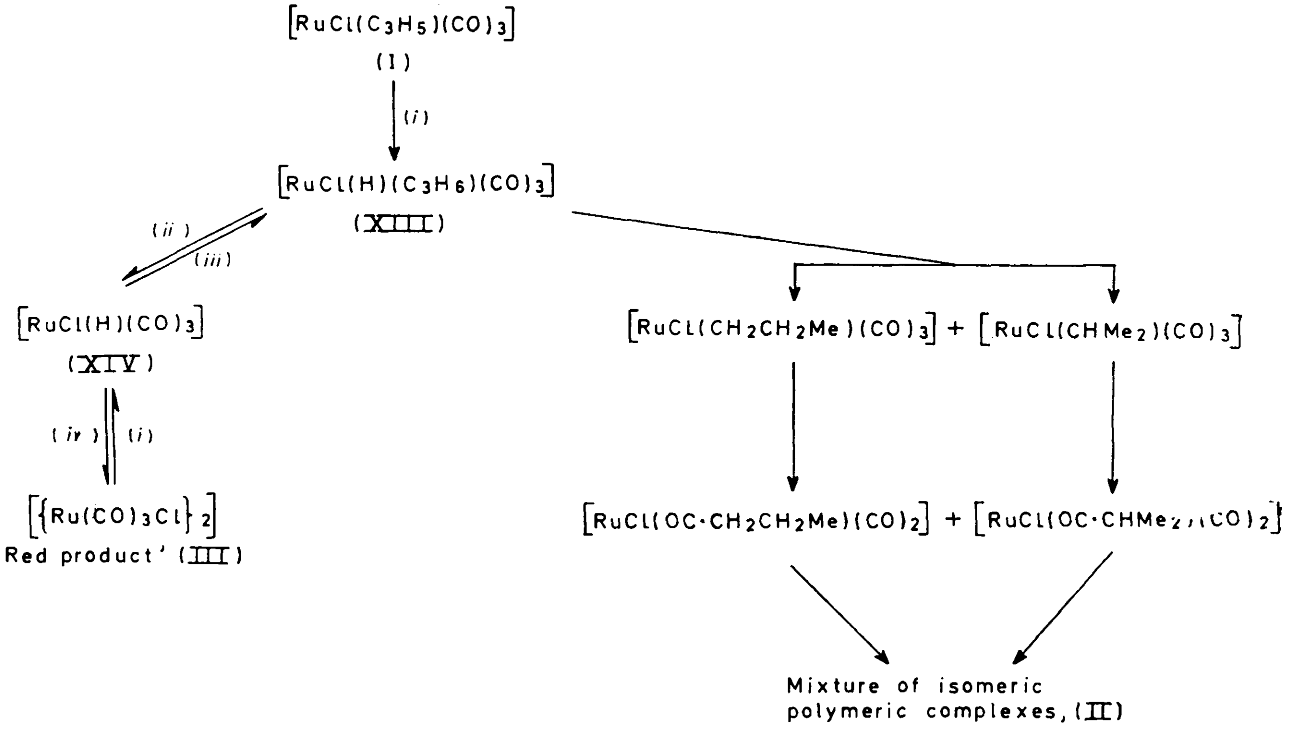
[23] D. Rose, J. D. Gilbert, R. P. Richardson, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 2610.

The dependence of the hydrogenation rate on the alkene concentration was studied, in the case of propene, carrying out a series of isochronous experiments varying the initial alkene concentration between 1·6 and 5·1 mol l^{-1} and keeping all other variables constant. The amount of propane formed within the same reaction time was linearly dependent on the initial alkene concentration (Figure 1), so indicating a first-order dependence on this variable. On the other hand, the hydrogenation rate seemed to approach an asymptotic value with increasing hydrogen pressure (Figure 2).

Another feature of (I) is its catalytic activity in the hydrogenation of aldehydes and ketones to alcohols. Under the same conditions used for the alkenes (100° C, 20—30 atm), acetone and n-butanal were converted to isopropyl alcohol and n-butanol, respectively, with a lower reaction rate with respect to that observed for the alkenes (20% conversion after 35 h using a catalyst concentration of 1·15mM).*



SCHEME 1 Interaction of [RuCl(C$_3$H$_5$)(CO)$_3$] with unsaturated substrates: (*i*) acn, −CO; (*ii*) EtO$_2$C·C⋮C·CO$_2$Et, −C$_3$H$_4$; (*iii*) PPh$_3$; (*iv*) RC⋮CR′; (*v*) C$_4$H$_6$



SCHEME 2 Suggested mechanism for the interaction of [RuCl (C$_3$H$_5$)(CO)$_3$] with hydrogen: (*i*) H$_2$; (*ii*) −C$_3$H$_6$; (*iii*) C$_3$H$_6$; (*iv*) −H$_2$

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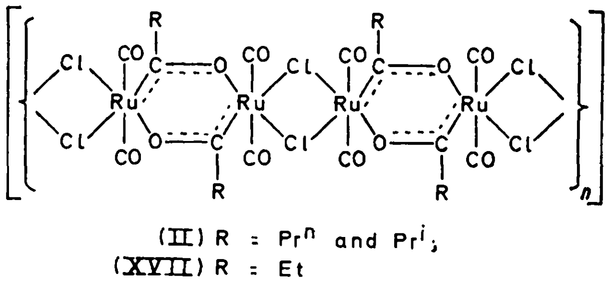
* 1M = 1 mol dm^{-3}.

To obtain information on the species involved in the catalytic hydrogenation of alkenes, an ethylene-hydrogenation experiment was stopped at low substrate conversion and attempts were made to ascertain the nature of the products present in solution. Hydrogen chloride was found in the reaction mixture and a dicarbonylchloro(propionyl)ruthenium species with C_2H_4 co-ordinated was detected by ^1H n.m.r. spectroscopy.[3] Attempts to isolate the ethylene complex failed and the polynuclear ' ethyl oxycarbene ' complex previously reported [3] was precipitated from the solution on adding n-pentane.

DISCUSSION

The reaction of (I) with unsaturated substrates (Scheme 1) can be explained, like other Group 8 metal–η-allyl systems, as occurring through a η–σ-perturbation of the η-allyl group and formation of highly reactive σ-allyl species which may undergo insertion reactions of the substrate co-ordinated to the metal.[14,15,24] The reaction with acrylonitrile, which results in the formation of a stable σ-allyl species containing the nitrile co-ordinated through the carbon–carbon double bond, clearly demonstrates this behaviour. A different course is observed for the reaction of alkynes which insert into the Ru–σ-allyl bond with formation of σ-acyl complexes (VII), (VIIIa), (VIIIb), and (IX) arising from migration of a 1,4-dienyl group on a CO group.

The course of the reaction of (I) with hydrogen and the ultimate formation of the mixture of two isomeric, polynuclear, bridging ' carbene ' complexes (II), analogous to those obtained by reaction of (I) with propene, and arising from hydrogenation and isomerisation of the allyl group, may be explained according to Scheme 2. Activation of hydrogen gives rise to an intermediate species (XIII) containing co-ordinated propene [25,26] from which bridging ' carbene ' groups of (II) may arise by Markownikoff and anti-Markownikoff insertion of the alkene into the Ru–H bond. In view of the similarity of the i.r. spectrum of (II) with that of the product obtained by treating (I) with propene [3] [apart from the bands due to the triple bridging OH and to benzene which are not present in (II)], the following polymeric arrangement is suggested:



(II) R = Pr^n and Pr^i;
(XVII) R = Et

On the other hand the '*red product*,' obtained on bubbling hydrogen through the hydrocarbon solution of (I) at 40—50 °C, may arise from (XIII) by release of gaseous propene and decomposition of the hydride (XIV) similar to some rhodium complexes.[27]

The catalytic behaviour of (I) in the hydrogenation and isomerisation of alkenes is quite different from that of other ruthenium hydrogenation catalysts such as $[RuCl(H)(PPh_3)_3]$ [21,22] and $[RuH(O_2CR)(PPh_3)_3]$ [23] which are selective for hydrogenation of alk-1-enes and only slightly active in the isomerisation reaction, especially in the absence of hydrogen. The rate-determining step, which, in the case of ruthenium–phosphine catalysts [21-23] is thought to be activation of hydrogen by oxidative addition to a square-planar alkyl complex, in the case of (I) seems to be alkene co-ordination to the metal in view of the experimentally observed first-order dependence on the alkene. In agreement with this conclusion, the experimental conditions under which (I) acts as an alkene-hydrogenation catalyst (*i.e.* 100 °C) are similar to those required for alkene activation (*i.e.* 70—80 °C),[3] whereas (I) activates hydrogen at much lower temperatures.

As regards the hydrogenation mechanism of ethylene, the presence in the reaction mixture of a dicarbonylchloro(propionyl)ruthenium species with co-ordinated ethylene, (XV) [3] (Scheme 3), and of hydrogen chloride suggests that just release of HCl from a hydrido-species, (XVI), allows the successive activation of the alkene and of hydrogen necessary for the catalytic hydrogenation. The reductive elimination of HCl instead of an aldehyde from (XVI) is in keeping with the low catalytic activity of (I) in the hydroformylation and carbonylation reactions that proceed rapidly only at high temperatures (150—200 °C).[2] Removal of ethylene and hydrogen from the solution, followed by addition of n-pentane, results in formation of the polymeric complex (XVII).

EXPERIMENTAL

η-Allylruthenium complexes, $[RuX(C_3H_5)(CO)_3]$ (X = Cl or Br), were prepared as previously described. All reagents were used as purchased; reactions were carried out under nitrogen. I.r. spectra were recorded on a Perkin-Elmer 225 spectrometer, ^1H n.m.r. spectra on a Varian T 60 instrument, and mass spectra on a Perkin-Elmer RMU-6H spectrometer; mass values are given for the ^{102}Ru isotope. M.p.s were measured in air on a Kofler hot-stage apparatus. U.v. spectra were recorded on a Cary 14 instrument. Microanalyses were by Dr. Nuti, Facoltà di Farmacia, Pisa. Molecular weights were determined on a Mechrolab apparatus.

Reactions of (*η-Allyl*)*tricarbonylchlororuthenium*.—(a) *With hydrogen under pressure*. The complex (0·31 g, 1·18 mmol) in benzene (10 cm^3), contained in an open glass vial, was treated with hydrogen (8 atm) in an autoclave for 15 h at 50 °C. From the solution a yellow *solid*, (II), separated on adding n-hexane; after washing with n-hexane the product was dried *in vacuo* (0·28 g); $\tau(C_6D_6)$ 8·8 (m, protons of CH_3 of Pr^n and Pr^i groups), 8·4 (m, protons of internal CH_2 of Pr^n), and 7·2 (m, protons of

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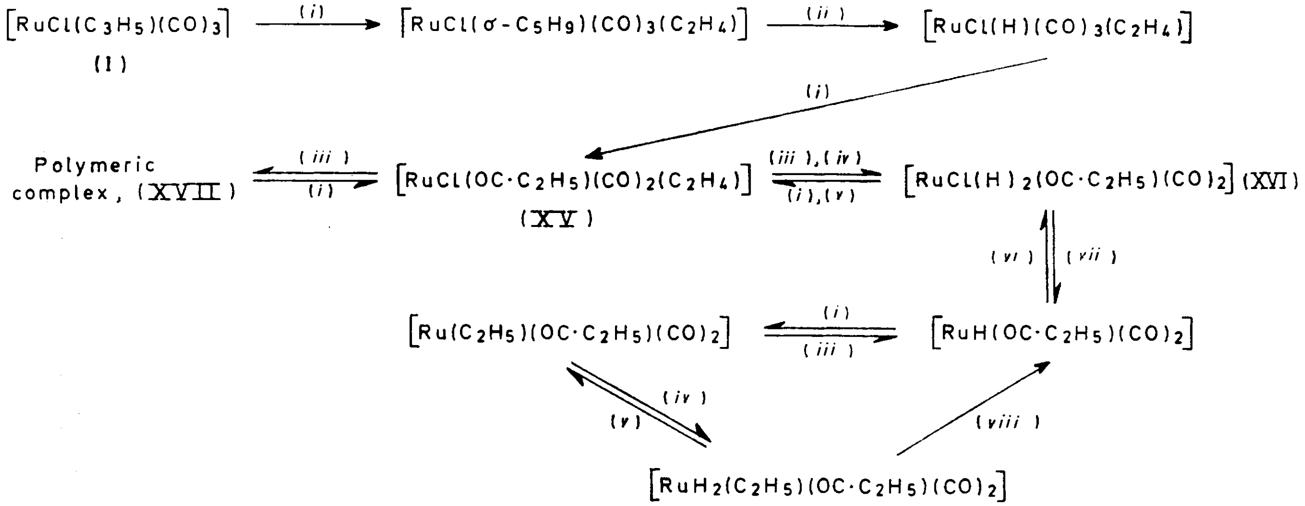
terminal CH_2 of Pr^n and of CH of Pr^i); $\nu_{max.}$ (KBr) at 2 978w, 2 940w, 2 875w, 2 130m (CO), 2 060s (CO), 1 998s (CO), 1 630vw, 1 540s (CO) (' carbene '), 1 455m, 1 395w, 1 380w, 1 365w, 1 270m, 1 205w, 1 170w, 1 108m, 985s, 888w, 850w, 810w, 630m, 610m, 570m, 500m, 460m, 323w (Ru–Cl) (terminal), 278m (Ru–Cl) (bridging), and 269m cm^{-1} (Ru–Cl) (bridging).

(b) *With hydrogen in a gas-volumetric apparatus.* The complex (0·49 g, 1·88 mmol) in iso-octane (15 cm^3) in a gas-volumetric apparatus was heated under hydrogen at atmospheric pressure for 60 h at 60 °C. Hydrogen was consumed (1·65 mmol) and a yellow *solid* was separated from the solution, washed with n-hexane, and dried *in vacuo.* I.r. and ^1H n.m.r. spectra were analogous to that of the product in (*a*).



SCHEME 3 Suggested mechanism for the hydrogenation of ethylene with $[RuCl(C_3H_5)(CO)_3]$: (*i*) C_2H_4; (*ii*) $-C_5H_8$; (*iii*) $-C_2H_4$; (*iv*) H_2; (*v*) $-H_2$; (*vi*) HCl; (*vii*) $-$HCl; (*viii*) $-C_2H_6$

(c) *On bubbling hydrogen through the solution.* Hydrogen was bubbled through a solution of the complex (0·5 g, 1,9 mmol) in n-hexane (25 cm^3) for 1 h at 40 °C. The *dark red product* which precipitated was filtered off, washed with n-pentane, and dried *in vacuo* (0·36 g) (Found: C, 16·65; Cl, 15·6. Calc. for $C_6Cl_2O_6Ru_2$: C, 16·3; Cl, 16·0%); $\nu_{max.}$ (KBr) at 2 033s (CO), 2 000s (CO), 1 965s (CO), 625m, 605w, 560m, 485m, and 260w cm^{-1} (Ru–Cl) (bridging); also present with a very low intensity were the bands of the product obtained in (*a*).

(d) *With triphenylphosphine.* A solution of triphenylphosphine (0·41 g, 1·57 mmol) and (η-allyl)bromotricarbonylruthenium (0·46 g, 1·5 mmol) in benzene (14 cm^3) was maintained at 55 °C for 6 h in a gas-volumetric apparatus. The carbon monoxide evolved was *ca.* 1 mol per mol of ruthenium. The solvent was removed *in vacuo* and the residue was crystallised from iso-octane to give yellow crystalline (*η-allyl*)*bromodicarbonyltriphenylphosphineruthenium,* (IV) (0·423 g, 52%), m.p. 134—135 °C [Found: C, 51·5; H, 3·95; Br, 14·8; *M*(benzene), 576. Calc. for $C_{23}H_{20}BrO_2PRu$: C, 51·1; H, 3·75; Br, 14·8%; *M*, 540·38].

(e) *With acrylonitrile.* Similarly, acrylonitrile (3·24 g, 61·3 mmol) and (η-allyl)tricarbonylchlororuthenium (0·35 g, 1·34 mmol) were reacted (13 h) in toluene (14 cm^3) at 80 °C. The carbon monoxide evolved was *ca.* 1 mol per mol of ruthenium. The solvent and excess of acrylonitrile were partially removed *in vacuo* and n-pentane was added. The resulting precipitate was filtered off, washed with n-pentane, and dried *in vacuo* to give pale yellow *di-μ-chloro-bis*[(*η-acrylonitrile*)(*σ-allyl*)*dicarbonylruthenium*], (V), insoluble in the common organic solvents (0·29 g, 77%) (Found: C, 33·2; H, 2·80; Cl, 11·8; N, 5·2. Calc. for $C_8H_8ClNO_2Ru$: C, 33·5; H, 2·80; Cl, 12·35; N,4·90%).

(f) *With acetylene.* The complex $[RuCl(C_3H_5)(CO)_3]$ (0·4 g, 1·53 mmol) in iso-octane, contained in an open glass vial, was treated with acetylene (6—10 atm) in an autoclave for 5 h at 80 °C. After cooling, the solvent was partially removed *in vacuo* and the resulting precipitate was filtered off, washed with n-pentane, and dried *in vacuo* to give yellow-brown *bis*[*dicarbonylchloro*(*hexa*-2,5-*dienoyl*)*ruthenium*], (VII) (0·23 g, 54%) [Found: C, 33·5; H, 2·75; Cl, 12·7; *M*(methyl ethyl ketone), 356. Calc. for $C_8H_7ClO_3Ru$: C, 33·4; H, 2·45; Cl, 12·3%; *M*, 287·7].

(g) *With phenylacetylene.* Phenylacetylene (0·93 g, 9·1 mmol) and $[RuCl(C_3H_5)(CO)_3]$ (0·5 g, 1·9 mmol) were reacted (4 h) in toluene (20 cm^3) at 60 °C. The solution was then cooled and the resulting precipitate collected, washed with toluene, and dried *in vacuo* to give a white product, a mixture of *bis*[*dicarbonylchloro*(3-*phenylhexa*-2,5-*dienoyl*)*ruthenium*], (VIIIa), and *bis*[*dicarbonylchloro*-(2-*phenylhexa*-2,5-*dienoyl*)*ruthenium*], (VIIIb) [Found: C, 46·6; H, 3·10; Cl, 9·15; Ru, 27·8; *M*(methyl ethyl ketone), 406. Calc. for $C_{14}H_{11}ClO_3Ru$: C, 46·2; H, 3·05; Cl, 9·75; Ru, 27·8%; *M*, 363·8].

(h) *With diphenylacetylene.* Diphenylacetylene (1·62 g, 9 mmol) and $[RuCl(C_3H_5)(CO)_3]$ (0·4 g, 1·5 mmol) were reacted (5 h) in iso-octane (15 cm^3) at 85—95 °C. The resulting precipitate was collected and recrystallised from benzene–n-pentane to give yellow *bis*[*dicarbonylchloro*(2,3-*diphenylhexa*-2,5-*dienoyl*)*ruthenium*], (IX) [Found: C, 54·35; H, 3·35; Cl, 8·15; *M*(methyl ethyl ketone), 377. Calc. for $C_{20}H_{15}ClO_3Ru$: C, 54·6; H, 3·45; Cl, 8·05%; *M*, 439·9].

(i) *With butadiene.* The complex $[RuCl(C_3H_5)(CO)_3]$ (0·25 g, 0·96 mmol) in benzene (20 cm^3), contained in an open glass vial, was treated with butadiene (10 atm) in an autoclave for 24 h at 70 °C. After cooling, on adding n-pentane, a white product was precipitated and recrystallised from benzene–n-pentane to give *tricarbonylchloro*(1—3-η-*pentadeca*-2,6,10,14-*tetraen*-1-*yl*)*ruthenium*, (X) [Found: C, 50·75; H, 5·40; Cl, 7·9. Calc. for $C_{18}H_{23}ClO_3Ru$: C, 51·0; H, 5·45; Cl, 8·35%].

(j) *With diethyl acetylenedicarboxylate.* A solution of diethyl acetylenedicarboxylate (0·55 g, 3·42 mmol) and $[RuCl(C_3H_5)(CO)_3]$ (0·3 g, 1·15 mmol) in iso-octane (15 cm³) were reacted (4 h) at 80 °C. The solvent was partially removed *in vacuo* and the crude product was separated as an oil and crystallised from methylene chloride–n-pentane to give [1,2-*bis*(*ethoxycarbonyl*)*vinyl*-2-*EtOCO*]*tricarbonylchlororuthenium*, (XI) (0·1 g, 25%) [Found: C, 33·9; H, 3·05; Cl, 8·65. Calc. for $C_{11}H_{11}ClO_7Ru$: C, 33·7; H, 2·85; Cl, 9·05]; *m/e* 392 (M^+), 364 ($M^+ - CO$), 336 ($M^+ - 2CO$), 308 ($M^+ - 3CO$), and 138 [$M^+ - 3CO - C_2H(CO_2Et)_2$].

(k) *With ethyl propiolate.* A solution of ethyl propiolate (0·5 g, 5·0 mmol) and $[RuCl(C_3H_5)(CO)_3]$ (0·4 g, 1·53 mmol) in iso-octane (15 cm³) were reacted (3 h) at 60 °C. The solution was cooled and the resulting precipitate collected, extracted with n-hexane, and dried *in vacuo* to give a dark yellow product, a mixture of *dicarbonylchloro*[3-*ethoxycarbonylhexa*-2,5-*dienoyl*]*ruthenium*, (XIIa), and *dicarbonylchloro*[2-*ethoxycarbonylhexa*-2,5-*dienoyl*]*ruthenium*, (XIIb) (0·26 g) (Found: C, 36·6; H, 3·20; Cl, 10·1. Calc. for $C_{11}H_{11}ClO_5Ru$: C, 36·8; H, 3·10; Cl, 9·90%].

Reaction of Product (II) *with Triphenylphosphine.*—In a gas-volumetric apparatus, product (II) (0·18 g) in benzene (10 cm³) was treated with triphenylphosphine (0·36 g, 1·37 mmol) at 60 °C for 6 h. Carbon monoxide was evolved and a yellow solid separated out on adding n-pentane. Recrystallisation of the product from benzene–n-pentane gave yellow-green crystals of a mixture of *butyrylcarbonylchlorobis*(*triphenylphosphine*)*ruthenium–benzene* and *carbonylchloro*(2-*methylpropionyl*)*bis*(*triphenylphosphine*)*ruthenium–benzene* (0·21 g) [Found: C, 66·65; H, 5·25; Cl, 4·25; *M*(benzene), 813·4. Calc. for $C_{47}H_{43}ClO_2P_2Ru$: C, 67·4; H, 5·15; Cl, 4·25%; *M*, 838·3].

Reaction of Complex (V) *with Triphenylphosphine.*—Di-μ-chloro-bis[(η-acrylonitrile)(σ-allyl)dicarbonylruthenium] (0·20 g, 0·7 mmol) and triphenylphosphine (0·55 g, 2·1 mmol) in benzene (30 cm³) were reacted (12 h) at 75 °C. The solvent was partially removed *in vacuo* and n-hexane was added. The resulting precipitate was filtered off and recrystallised from benzene–n-pentane to give white (η-*acrylonitrile*)(σ-*allyl*)*dicarbonylchlorotriphenylphosphineruthenium* (VI) (Found: C, 57·7; H, 4·20; Cl, 6·95; N, 2·30. Calc. for $C_{26}H_{23}ClNO_2PRu$: C, 56·9; H, 4·20; Cl, 6·45; N, 2·55%).

Reaction of Product (II) *with Iodine and Methanol.*—Product (II) (0·15 g) was treated with a methanolic solution (2 cm³) of iodine (0·2M) at 60 °C for 2 h. G.l.c. analysis (di-n-decyl phthalate on Celite) demonstrated the formation of methyl n-butyrate and isobutyrate.

Reaction of Product (II) *with Carbon Monoxide and Methanol.*—Product (II) (0·25 g) in methanol (4 cm³) was treated in an autoclave with carbon monoxide (50 atm) at 100 °C for 4 h. G.l.c. analysis (see above) demonstrated the presence of the two above mentioned esters.

Hydrogenation and Isomerisation Experiments.—The reactions were normally carried out in stainless-steel autoclaves (125 cm³). Each reaction was performed at least twice in different autoclaves. Substrates were freed from peroxides by passage through a 30 cm column of activated alumina followed by fractional distillation from sodium under nitrogen. The boiling range of the fractions used was: cyclohexene 84—85, hex-1-ene 63—64, *cis*- + *trans*-hex-2-ene 68—69 °C (Fluka, A.G.); but-1-ene, ethylene and propene (Montedison, trap distilled only).

In a typical experiment the autoclave, charged with the catalyst, was flushed with dry nitrogen and evacuated twice. Toluene and the alkene were charged by suction and then the autoclave, heated at 100 °C in an oil-bath with agitation, was compressed with hydrogen to the required level. After the reaction the vessel was cooled rapidly and the products analysed immediately by g.l.c. In the hydrogenation experiments the hydrogen pressure was kept constant at the desired value (±2%) by introduction of hydrogen from a high-pressure vessel. In all reactions air was excluded and solvents purified and degassed.

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