A Kinetic Study on Asymmetric Transfer Hydrogenation of Unsaturated Acids and Esters by Alcohols with Binuclear Ruthenium(II) Chiral Diphosphine Complexes

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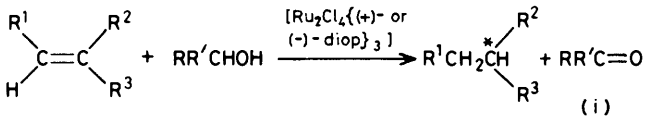
Kinetic investigation of the $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ [diop = 2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane] catalysed transfer hydrogenation of unsaturated acids and esters by alcohols indicated that the catalytically active $[RuCl_2\{(-)\text{-diop}\}]$ complex generated from the $[Ru_2Cl_4\{(-)\text{-diop}\}_3] \rightleftharpoons [RuCl_2\{(-)\text{-diop}\}] + [RuCl_2\{(-)\text{-diop}\}_2]$ reaction afforded chiral hydrogenated products *via* the reaction of a hydrogen acceptor–$[RuCl_2\{(-)\text{-diop}\}]$ (hydrogen donor) complex and of a hydrogen donor–$[RuCl_2\{(-)\text{-diop}\}]$ (hydrogen acceptor) complex. ^{31}P N.m.r. analysis of $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ in solution also suggested the possibility of $[RuCl_2\{(-)\text{-diop}\}_3]$ formation from $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$. The reaction mechanism is also discussed on the basis of isotope effects observed in the $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ catalysed reaction between deuteriated benzyl alcohols and unsaturated species.

Studies of catalytic enantiomer-differentiating reactions with chiral transition metal complexes have centred around the asymmetric hydrogenation of prochiral unsaturated species, and rhodium(I) chiral phosphine complexes have been accepted as efficient catalysts for asymmetric hydrogenation reactions. In this respect, complexes of ruthenium with chiral phosphines have hitherto been objects of only limited investigation in asymmetric reactions, although some examples of asymmetric hydrogenation of olefins by ruthenium(II) chiral phosphine complexes have been documented previously.[1] In our laboratory, a binuclear chiral ruthenium(II) complex, $[Ru_2Cl_4\{(+)\text{- or } (-)\text{-diop}\}_3]$, was found to be an efficient catalyst for the asymmetric transfer hydrogenation of prochiral unsaturated substrates by alcohols [equation (i)].[2] For example, $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ offered a 26.4% enantiomer excess of (−)-(*R*)-α-methylbutyric acid in the transfer hydrogenation of (*E*)-α-methylcrotonic acid by 1-phenylethanol at 170 °C,[2c] and the enantioselective dehydrogenation of RR′CHOH was also realized by the use of racemic secondary alcohols as hydrogen source.[2a,b]

The chiral ruthenium complex $[H_4Ru_4(CO)_8\{(-)\text{-diop}\}_2]$ has also been reported as an efficient catalyst for the asymmetric transfer hydrogenation of prochiral ketones by secondary alcohols; a maximum enantiomer excess of 9.8% was obtained in the reaction of $PhCOCH_2CHMe_2$ and Me_2CHOH at 120 °C.[3] However, the mechanism of asymmetric transfer hydrogenation, including the structure of the catalytically active species formed from binuclear or cluster-type ruthenium complexes, has not yet been elucidated, even though there are some kinetic studies on the transfer hydrogenation of olefins or aldehydes by a hydrogen donor (alcohol, indole, or dioxane) with $[RhCl(PPh_3)_3]$,[4] $[RuCl_2(PPh_3)_3]$,[5] or $[RuH_2(PPh_3)_3]$.[6] We have now investigated the mechanism of $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ catalysed asymmetric transfer hydrogenation of unsaturated acids and esters by alcohols, with particular reference to the structure of the catalytically active species.

Experimental

Materials.—The binuclear ruthenium(II) complex $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ was prepared from $[RuCl_2(PPh_3)_3]$ and (−)-diop according to the reported method.[2] $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$



(i)

showed δ_H ($CDCl_3$) 0.86 (s, 6 H), 1.57 (br, 12 H), 3.02 (br, 6 H), 6.98 (m, 20 H), and 7.18 (m, 4 H) (Found: C, 60.8; H, 5.75; Cl, 7.6. Calc. for $C_{93}H_{96}Cl_4P_6Ru_2$: C, 60.7; H, 5.2; Cl, 7.2%). 1-Phenylethyl (*E*)-α-methylcrotonate was obtained by the reaction of 1-phenylethanol and (*E*)-α-methylcrotonoyl chloride, and deuteriated benzyl alcohols were prepared by the reported method.[7] Other commercially available organic materials were purified by fractional distillation or recrystallization before use.

Transfer Hydrogenation.—Transfer hydrogenation of (*E*)-α-methylcrotonic acid (0.38—1.75M) or 1-phenylethyl (*E*)-α-methylcrotonate (0.18—0.76M) by 1-phenylethanol (1.0—7.5M) in diphenyl ether was carried out with $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ (0.75—5mM) in a sealed tube at 140—200 °C under nitrogen. The amounts of unchanged substrate and hydrogenated product were measured by g.l.c. analysis (at 170 °C using a 1 m column packed with 15% EGA on Uniport B) or by 100 MHz ^1H n.m.r. analysis. The transfer hydrogenation of 2.5M-unsaturated acids [(*E*)-α-methylcrotonic and (*E*)-α-methylcinnamic acids] or 2.5M-unsaturated esters [ethyl (*E*)-α-methylcrotonate and (*E*)-α-methylcinnamate] by deuteriated benzyl alcohols ($PhCH_2OD$, $PhCD_2OH$, $PhCD_2OD$, and/or $PhCH_2OH$) was performed with 5mM$[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ at 190 °C under nitrogen; the distribution of deuterium recovered hydrogen donors and hydrogenated products was determined by means of 100 MHz ^1H n.m.r. spectroscopy.

Results and Discussion

Rate Dependence on Concentration of Catalyst, Alcohol, and Unsaturated Substrate.—As indicated by typical time–yield curves for the present $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ catalysed transfer hydrogenation (Figure 1), the conversion of the unsaturated substrate into the hydrogenated product is linear with time

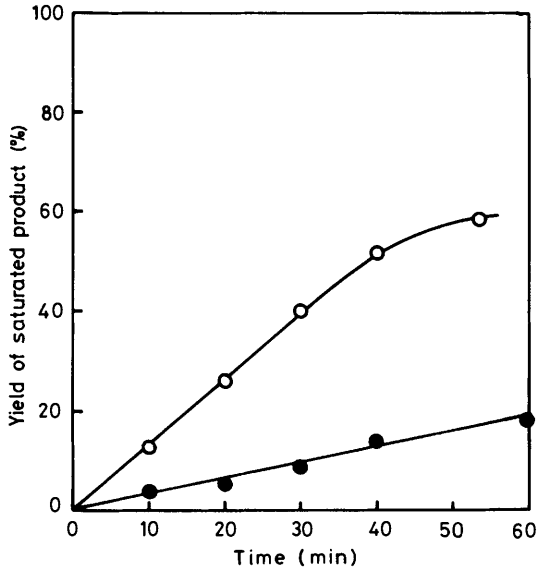


Figure 1. Typical time–yield curves for the $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ (1 mmol dm^{-3}) catalysed hydrogenation of (*E*)-α-methylcrotonic acid (0.63 mol dm^{-3}) (○) at 150 °C, and of 1-phenylethyl (*E*)-α-methylcrotonate (0.50 mol dm^{-3}) (●) at 165 °C by 1-phenylethanol (7.0 mol dm^{-3}) in Ph_2O

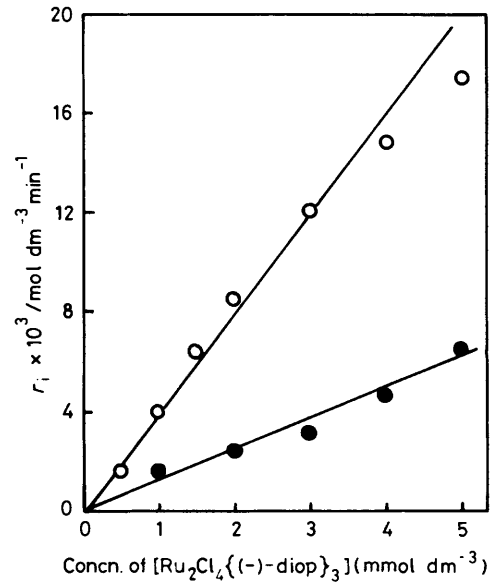


Figure 2. Dependence of the initial rate (r_i) on the concentration of $[Ru_2Cl_2\{(-)\text{-diop}\}_3]$ in the transfer hydrogenation of (*E*)-α-methylcrotonic acid (0.80 mol dm^{-3}) by 1-phenylethanol (7.5 mol dm^{-3}) at 150 °C and of 1-phenylethyl (*E*)-α-methylcrotonate (0.50 mol dm^{-3}) at 165 °C by 1-phenylethanol (6.5 mol dm^{-3}) in Ph_2O (symbols as in Figure 1)

during the initial stage; when an unsaturated acid was used as hydrogen acceptor, the reaction proceeded stoicheiometrically up to more than 20% conversion at temperatures below 190 °C, but thereafter some of the hydrogen donor was consumed by the esterification reaction with the saturated acids (the extent of the esterification reaction between such alcohols as 1-phenylethanol and unsaturated acids was negligibly small, especially during the initial reaction stage). The initial reaction rate (r_i), derived from the linear part of the time–yield curve, was directly proportional to the concentration of the $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ catalyst and to that of the hydrogen donor (Figures 2 and 3). The first-order dependence of the reaction rate on the concentration of $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ and that of the hydrogen donor suggests that $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ itself changes into a catalytically active species, to which one hydrogen-donor molecule co-ordinates for reaction. Although a linear dependence of the reaction rate on the concentration of hydrogen acceptor was observed in the case of unsaturated esters, the initial rate was reduced with increasing concentrations of unsaturated acid, and a linear relationship between $1/r_i$ and the concentration of the unsaturated acid was established, with a positive intercept on the vertical axis (Figure 4). The unsaturated acid co-ordinates to the Ru^{II} complex easily and strongly, as compared with the unsaturated ester, which might retard the co-ordination of hydrogen donor *via* shielding of the active co-ordination site of the catalyst.

Rate Dependence on Added (−)-diop Concentration and Reaction Temperature.—The addition of (−)-diop to the reaction system reduced the initial rate (r_i), and the plots of $1/r_i$ *vs.* added (−)-diop concentration tend towards a straight line with a positive intercept (Figure 5). The co-ordination of added (−)-diop to the catalytically active species (which will be discussed later) makes the catalyst inactive, but the co-ordination strength of (−)-diop is not very much larger than that of the hydrogen donor or acceptor, as can be seen from the rate decrease on addition of (−)-diop (Figure 5). The initial rate was also influenced by the reaction temperature (140—200 °C), and the plots of $\ln(r_i)$ *vs.* $1/T$ gave linear Arrhenius relationshionships for the present transfer hydrogenation of the unsaturated acid and ester (Figure 6). Therefore, the present reaction proceeds *via* the same mechanism in the temperature range of 140—200 °C without structural change in the catalytically active species. With regard to the activation parameters, the activation energy E_a, enthalpy of activation $\Delta H^{\ddagger}$, and entropy of activation $\Delta S^{\ddagger}$ were evaluated as 22.8 [23.9] kcal mol^{-1}, 22.0 [23.1] kcal mol^{-1}, and −13.7 [−18.9]

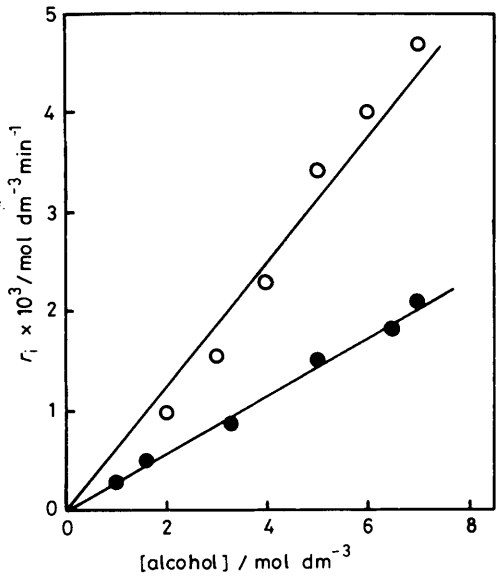


Figure 3. Dependence of the initial rate (r_i) on the concentration of 1-phenylethanol in the $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ catalysed transfer hydrogenation of (*E*)-α-methylcrotonic acid (0.80 mol dm^{-3}) at 150 °C, and of 1-phenylethyl (*E*)-α-methylcrotonate (0.50 mol dm^{-3}) at 165 °C in Ph_2O (symbols as in Figure 1)

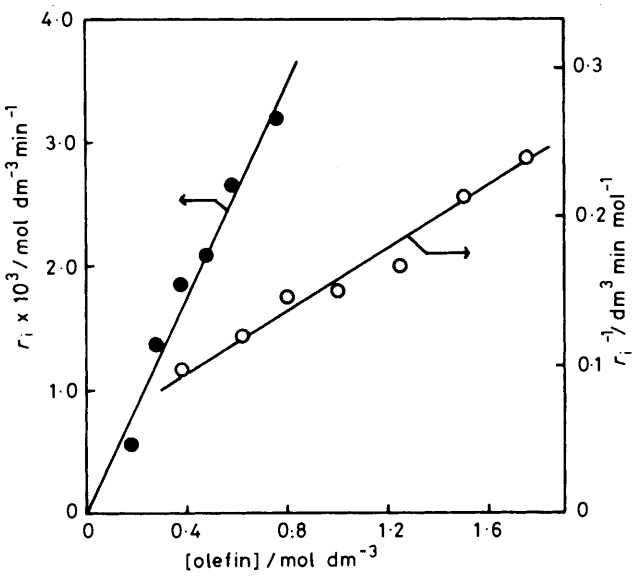


Figure 4. Dependence of the initial rate (r_i) on the olefin concentration in the [Ru_2Cl_4\{(−)-diop\}$_3$] catalysed transfer hydrogenation of (*E*)-α-methylcrotonic acid (○) at 150 °C and of 1-phenylethyl (*E*)-α-methylcrotonate (●) at 165 °C by 1-phenylethanol in Ph_2O; (alcohol 7.0 mol dm^{-3}, [Ru_2Cl_4\{(−)-diop\}$_3$] 1 mmol dm^{-3})

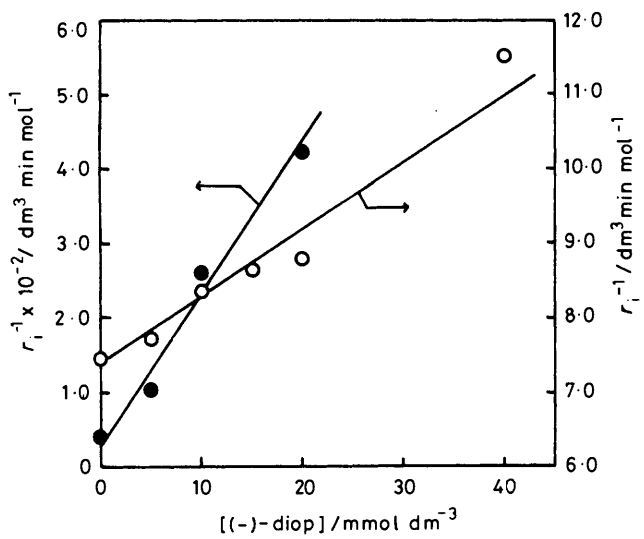


Figure 5. Dependence of the initial rate (r_i) on the concentration of added (−)-diop in the [Ru_2Cl_4\{(−)-diop\}$_3$] (1 mmol dm^{-3}) catalysed transfer hydrogenation of (*E*)-α-methylcrotonic acid (0.80 mol dm^{-3}) (○) at 150 °C, and of 1-phenylethyl (*E*)-α-methylcrotonate (0.50 mol dm^{-3}) (●) at 190 °C by 1-phenylethanol (7.5 mol dm^{-3}) in Ph_2O

cal mol^{-1} K^{-1} for the [Ru_2Cl_4\{(−)-diop\}$_3$] catalysed transfer hydrogenation of (*E*)-α-methylcrotonic acid [1-phenylethyl (*E*)-α-methylcrotonate] by 1-phenylethanol. Although the transfer hydrogenation of the bulky unsaturated ester required a slightly larger activation energy as compared with that of the unsaturated acid, the present reaction is considered to proceed *via* the process shown in Scheme 1, where (Ru) denotes a catalytically active species; the participation of H^+ in the reaction process has been confirmed by Sasson and Blum.[5]

Generation of Catalytically Active Species.—It is necessary here to discuss the catalytically active species formed from the

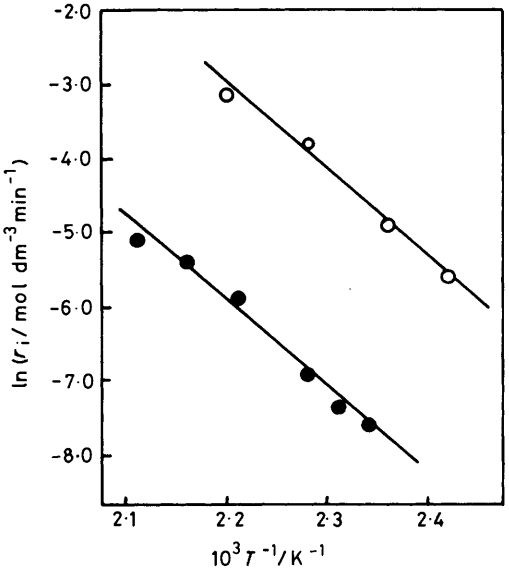


Figure 6. Plots of ln(r_i) *vs.* T^{-1} for the [Ru_2Cl_4\{(−)-diop\}$_3$] catalysed transfer hydrogenation of (*E*)-α-methylcrotonic acid (○) and 1-phenylethyl (*E*)-α-methylcrotonate (●) by 1-phenylethanol in Ph_2O (catalyst 1 mmol dm^{-3}, olefin 0.50 mol dm^{-3}, alcohol 7.4 mol dm^{-3})

binuclear ruthenium(II) diphosphine complex, [Ru_2Cl_4\{(−)-diop\}$_3$]. The ^{31}P n.m.r. spectrum of [Ru_2Cl_4\{(−)-diop\}$_3$] at 40.32 MHz (*o*-$Cl_2C_6H_4$ at −10 °C with external standard 85% H_3PO_4 in D_2O) showed six different peaks, one due to free (−)-diop (−24.6 p.p.m.) and five others denoted a (13.4 p.p.m.), b (21.0 p.p.m.), c (29.7 p.p.m.), d (37.4 p.p.m.), and e (67.6 p.p.m.), in the ratios 1.5 : 1 : 3 : 3 : 1 : 4 with J_{PP} 28.1 (doublet a), 28.1 (doublet b), 35.4 (doublet c), 34.1 (doublet d), 31.9 (triplet e), and 33.9 Hz (triplet e) as shown in Figure 7. Since the remarkable difference in the chemical shifts (a—b 306 Hz, b—c 351 Hz, and c—d 310 Hz) does not correspond to the usual P–P coupling (J_{PP} 25—40 Hz)[8] [there is no Ru(quadrupolar nuclear)–P coupling], the chemical shifts indicate the mixtures of relatively stable five- or six-co-ordinate ruthenium(II) complexes generated from [Ru_2Cl_4\{(−)-diop\}$_3$] *via* the equilibrium reactions shown in Scheme 2, where the co-ordination of one solvent molecule to the five-co-ordinated Ru^{II} complexes is assumed. Since peaks c, d, and e change into one broad signal (51.0 p.p.m.) on raising the temperature from −10 to 70—100 °C, they can be assigned to diop in [Ru_2Cl_4\{(−)-diop\}$_2$], terminal diop in [Ru_2Cl_4\{(−)-diop\}$_3$]], and bridging diop in [Ru_2Cl_4\{(−)-diop\}$_3$], respectively, and peaks a and b could well be those of diop in the two stable isomers of [$RuCl_2$\{(−)-diop\}] (tetrahedral or square planar).

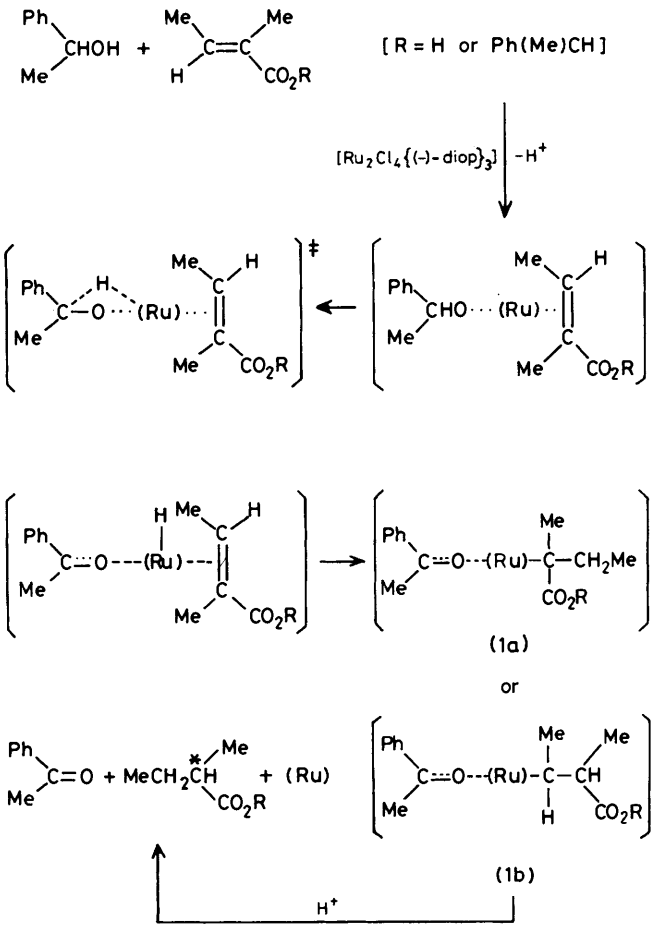
Thus, three different Ru^{II} complexes: [$RuCl_2$\{(−)-diop\}], [$RuCl_2$\{(−)-diop\}$_2$], and [Ru_2Cl_4\{(−)-diop\}$_2$], can be produced from [Ru_2Cl_4\{(−)-diop\}$_3$] as shown in equations (ii);

$$[Ru_2Cl_4\{(-)\text{-diop}\}_3] \rightleftharpoons 2[RuCl_2\{(-)\text{-diop}\}] + (-)\text{-diop} \quad \text{(iia)}$$

$$[Ru_2Cl_4\{(-)\text{-diop}\}_3] \rightleftharpoons [Ru_2Cl_4\{(-)\text{-diol}\}_2] + (-)\text{-diop} \quad \text{(iib)}$$

$$[Ru_2Cl_4\{(-)\text{-diop}\}_3] \rightleftharpoons [RuCl_2\{(-)\text{-diop}\}] + [RuCl_2\{(-)\text{-diop}\}_2] \quad \text{(iic)}$$

the unstable four-co-ordinate complexes might include solvent as a ligand.



Scheme 1.

The catalytically active species [$RuCl_2${(−)-diop}] is then generated *via* reaction (iia) or (iic).

Reaction Mechanism.—If the catalytically active [$RuCl_2$-{(−)-diop}] complex is generated *via* reaction (iia), the mechanism shown in Scheme 3 can be considered, where cat = [Ru_2Cl_4{(−)-diop}$_3$], L = (−)-diop, R = catalytically active [$RuCl_2${(−)-diop}], S = unsaturated substrate, and D = alcohol.

A stationary-state assumption applied to [R·S] and [R·D] affords the rate equation (iiia) for product formation. From

$$r = k_5[R\cdot S][D] + k_6[R\cdot D][S] = (k_5K_2 + k_6K_4)(K_1[cat]/[L])^{\ddagger}[D][S] \quad \text{(iiia)}$$

the material balance: $[cat]_0 = [cat] + ([R] + [R\cdot S] + [R\cdot D] + [R\cdot S_2])/2 = [cat] + [cat]^{\ddagger}(1 + K_2[S] + K_4[D] + K_2K_3[S]^2) \times (k_1/4[L])^{\ddagger}$, the rate equation (iiia) can be rewritten in two different ways. The case $[cat] \ll [cat]^{\ddagger}(1 + K_2[S] + K_4[D] + K_2K_3[S]^2) \times (K_1/4[L])^{\ddagger}$ {*i.e.* $([R] + [R\cdot S] + [R\cdot D] + [R\cdot S_2])/2 \gg [cat]$} gives (iiib), and the case $[cat] \gg [cat]^{\ddagger}(1 + K_2[S] + K_4[D] + K_2K_3[S]^2) \times (K_1/4[L])^{\ddagger}$ {*i.e.* $([R] + [R\cdot S] + [R\cdot D] + [R\cdot S_2])/2 \ll [cat]$} gives (iiic).

$$r = 2(k_5K_2 + k_6K_4)[cat]_0[S][D]/(1 + K_2[S] + K_4[D] + K_2K_3[S]^2) \quad \text{(iiib)}$$

$$r = (k_5K_2 + k_6K_4)[S][D](K_1[cat]_0/[L])^{\ddagger} \quad \text{(iiic)}$$

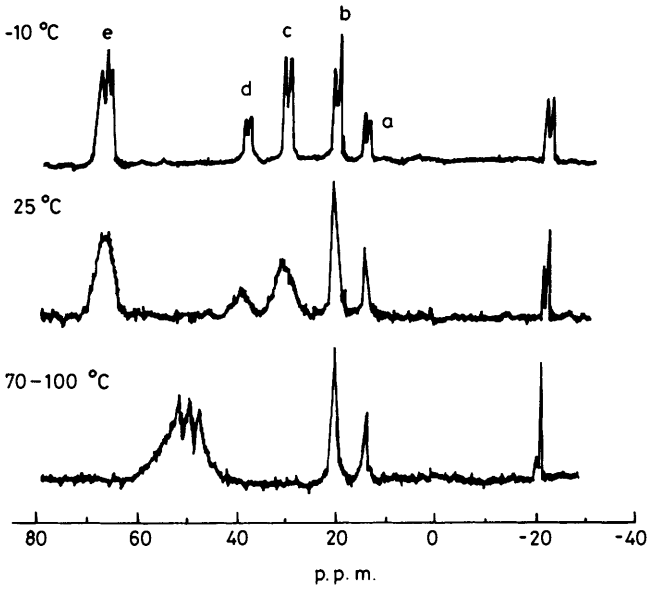


Figure 7. ^{31}P N.m.r. spectrum of $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$

Although the first-order dependence of r_1 on $[cat]_0$ is explained not by equations (iiia) and (iiic) but by (iiib), the linear relation between $1/r_1$ and [L] is not recognized from any of equations (iiia—c). Therefore, Scheme 3 can be discarded as unacceptable.

If the catalytically active [$RuCl_2${(−)-diop}] complex is formed in reaction (iic), the mechanism can be expressed as in Scheme 4, where cat = [Ru_2Cl_4{(−)-diop}$_3$], A = [$RuCl_2${(−)-diop}$_2$], R = [$RuCl_2${(−)-diop}], S = unsaturated substrate, and D = alcohol.

The rate equation derived from the stationary-state assumption applied to [R·S] and [R·D] is (iva). From the

$$r = K_3[R\cdot S][D] + k_6[R\cdot D][S] = K_1(k_5K_2 + k_6K_4)[cat][S][D]/[A] \quad \text{(iva)}$$

relation $[cat]_0 = [cat] + [R] + [R\cdot S] + [R\cdot D] + [R\cdot S_2] = ([A] + K_1 + K_1K_2[S] + K_1K_4[D] + K_1K_2K_3[S]^2)[cat]/[A]$, the rate equation can be rewritten as (ivb). When the substrate

$$r = (k_5K_2 + k_6K_4)[cat]_0[S][D]/([A]/K_1 + 1 + K_2[S] + K_4[D] + K_2K_3[S]^2) \quad \text{(ivb)}$$

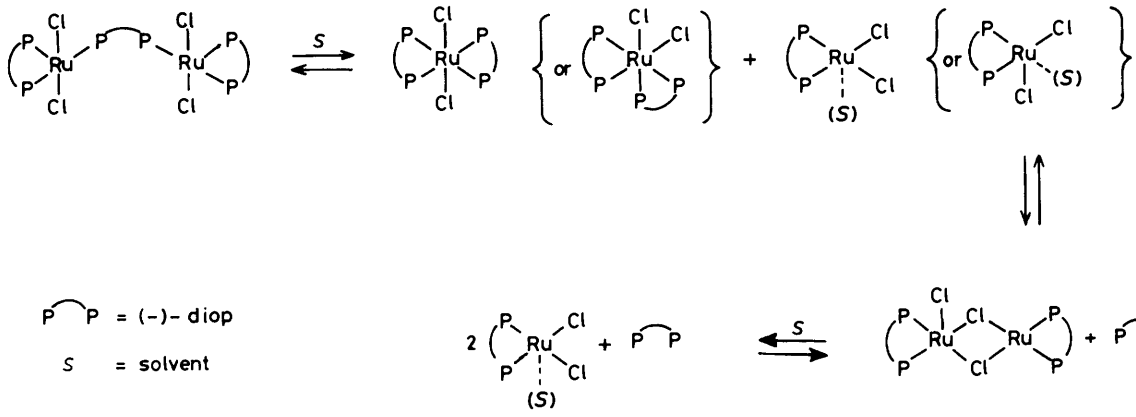
(S) is an unsaturated acid such as (*E*)-α-methylcrotonic acid, the linear relationship between $1/r_1$ and [S] requires $[A]/K_1 + 1 + K_4[D] \ll K_2[S] + K_2K_3[S]^2$ {*i.e.* $[cat] + [R] + [R\cdot D] \ll [R\cdot S] + [R\cdot S_2]$}, so that the rate equation is (ivc), where $k' = (k_5K_2 + k_6K_4)/K_2$.

$$r = k'[cat]_0[D]/(1 + K_3[S]) \quad \text{(ivc)}$$

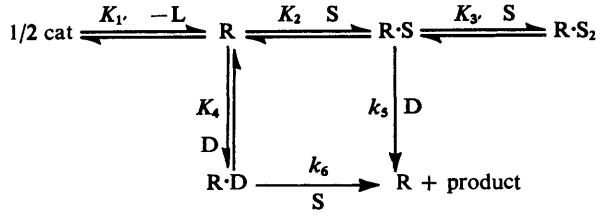
When the substrate S is an unsaturated ester such as 1-phenylethyl (*E*)-α-methylcrotonate, the linear relation between r_1 and [S] requires $[A]/K_1 + 1 \gg K_2[S] + K_4[D] + K_2K_3[S]^2$ {*i.e.* $[cat] + [R] \gg [R\cdot S] + [R\cdot D] + [R\cdot S_2]$}, so that the rate equation can be expressed as (ivd), where

$$r = k''[cat]_0[S][D]/([A]/K_1 + 1) \quad \text{(ivd)}$$

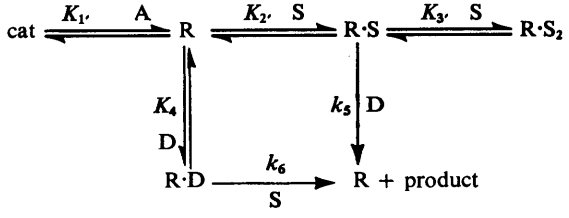
$k'' = k_5K_2 + k_6K_4$. Both rate equations (ivc and d) reflect the linear relation of r_1 *vs.* $[cat]_0$ and of r_1 *vs.* [D].



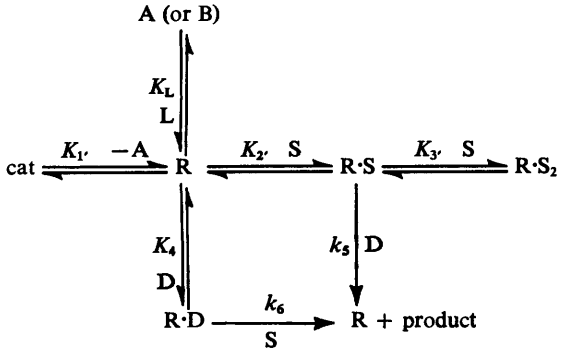
Scheme 2.



Scheme 3.



Scheme 3.



Scheme 4'.

In order to discuss the effect of addition of (−)-diop on the reaction rate, it is necessary to rewrite Scheme 4 as Scheme 4', where L = (−)-diop, A = $[RuCl_2\{(-)\text{-diop}\}_2]$, and B = $[RuCl_2\{(-)\text{-diop}\}_2]$ but with a different structure from A.

The rate equation of Scheme 4' is given as (v). Since this

$$r = (k_5K_2 + k_6K_4)[\text{cat}]_0[S][D]/[A]/(K_1 + K_1[L] + K_2[S] + K_4[D] + K_2K_3[S]^2) \quad (v)$$

satisfies the linear relation between $1/r_1$ and [L] [(L) = (−)-diop] in addition to other linear relations mentioned above, the mechanism of the present reaction can be expressed by Scheme 4'.

Isotope Effects.—In order to define the reaction mechanism more precisely, the $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ catalysed transfer hydrogenation of (*E*)-α-methylcrotonic acid by a deuteriated benzyl alcohol ($PhCD_2OD$) was examined at 190 °C. The reaction rate (r_1^D) is lower than that (r_1^H) in the same reaction with $PhCH_2OH$, and the value of r_1^D/r_1^H (2.4) indicated the occurrence of rate-determining abstraction of hydrogen bound to α-carbon of the hydrogen source by the Ru^{II} complex catalyst, as suggested previously.[5] Such an isotope effect was also observed in the transfer hydrogenation of (*E*)-α-methylcrotonic and (*E*)-α-methylcinnamic acids and/or their ethyl esters (Table 1). It is notable that the deuteriated hydrogen source $PhCD_2OH$ resulted in a predominance of deuterium distribution in $MeCDH\overset{*}{C}H(Me)CO_2R$ or $PhCDH\overset{*}{C}H(Me)CO_2R$ (R = H or Et) rather than in $MeCH_2\overset{*}{C}D(Me)CO_2R$ or $PhCH_2\overset{*}{C}D(Me)CO_2R$. This suggests the preferential formation of [PhCDO · · · (Ru)–C(Me)–$(CO_2R)CDHR'$ (R' = Me or Ph)] as intermediate [*cf.* (1a) in Scheme 1], which might be stabilized by π-conjugation of the (Ru)–CCO_2R bond.[9] On the other hand, the deuteriated products $MeCDH\overset{*}{C}H(Me)CO_2R$ and $PhCDH\overset{*}{C}H(Me)CO_2R$ was also observed to the extent of 18—27%, even in the case when $PhCH_2OD$ was used. This is attributable to the irreversible formation of PhCDHOH from $PhCH_2OD$ *via* $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ catalysed intramolecular hydrogen–deuterium exchange in the deuterium source.[10] When $PhCH_2OD$ was heated at 190 °C for 6 h in the presence of 5.7M-$[Ru_2Cl_4\{(-)\text{-diop}\}_3]$, 29% of the deuterium was exchanged, with the formation of benzaldehyde and dibenzyl ether.

With regard to the enantiomer-differentiating process in the present reaction, there are two possible steps, *viz.* (*a*) selection of one face or the other during the co-ordination of a prochiral unsaturated substrate to the Ru^{II} complex catalyst, and (*b*) enantioselective product development during the protonation of a σ-type Ru^{II}–substrate complex [(1a) in Scheme 1]. If the former process is acceptable, the bulky substituent of the ester group in the substrate would retard the approach of the substrate to the Ru^{II} complex so as to decrease the extent of asymmetric induction. In the $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ catalysed transfer hydrogenation of $MeCH{=}C(Me)CO_2R$ (R = H, Me,

Table 1. $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ catalysed transfer hydrogenation of unsaturated acids and esters by deuteriated benzyl alcohols at 190 °C [a]

Unsaturated species	Alcohol [b]	Time (h)	Yield (%)	Deuterium distribution in product (%) Methine (CD)	Methylene (CDH)
$MeCH{=}CMeCO_2H$	$PhCH_2OD$	12	75	6	25
	$PhCD_2OH$	12	37	18	52
$MeCH{=}CMeCO_2Et$	$PhCH_2OD$	3	89	11	20
	$PhCD_2OH$	4	54	10	84
$PhCH{=}CMeCO_2H$	$PhCH_2OH$	24	47	0	0
	$PhCH_2OD$	24	32	7	18
	$PhCD_2OH$	24	25	43	91
	$PhCD_2OD$	24	23	43	96
$PhCH{=}CMeCO_2Et$	$PhCH_2OD$	12	27	14	27

[a] $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ concn. = 5.0×10^{-3} mol dm^{-3}, [unsaturated species] = 2.5 mol dm^{-3} in the alcohol. [b] Deuterium contents of alcohols are $PhCH_2OD$ (98%), $PhCD_2OH$ (81%), and $PhCD_2OH$ (81% in CD_2).

Table 2. $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ catalysed transfer hydrogenation of (*E*)-α-methylcrotonic acid and esters by 1-phenylethanol at 190 °C [a]

$MeCH{=}C(Me)CO_2R$ R	Time (h)	Yield (%)	$[\alpha]_D^{23}$/°	e.e.[b] (%) (config.)
H [c]	10	13	−3.21	26.4 (*R*)
H	4	10	−2.21	18.2 (*R*)
Me	3	85	−1.21	10.0 (*R*)
Et	22	59	−1.19	9.8 (*R*)
$PhCH_2$	5	75	−1.02	8.4 (*R*)
PhCHMe	10	71	+0.10	0.8 (*S*)

[a] $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ concn. = 4.0×10^{-3} mol dm^{-3}, [1-phenylethanol] = 6.7×10^{-2} mol dm^{-3}, [substrate] = 3.3×10^{-2} mol dm^{-3}. [b] Enantiomer excess calculated with respect to the following value of optically pure acid after hydrolysis of the esters: $[\alpha]_D^{23}$ +12.17 (*c* 5, EtOH) for (+)-(*S*)-$MeCH_2CHMeCO_2H$.[11] [c] At 170 °C.

Et, $PhCH_2$, or PhCHMe) by 1-phenylethanol at 190 °C, the enantiomer excess of the saturated product decreased in the order R = H > Me > Et > $PhCH_2$ > PhCHMe (Table 2). Therefore, selection of face plays a predominant role in the enantiomer-differentiating process of the present reaction.

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