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THE KINETICS AND MECHANISM OF HOMOGENEOUS HYDROGEN TRANSFER FROM ALCOHOLS TO BENZYLIDENEACETONE CATALYZED BY DICHLOROTRIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II)

GÁBOR SPEIER and LÁSZLÓ MARKÓ

Department of Organic Chemistry, Veszprém University of Chemical Engineering, 8201 Veszprém (Hungary)

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Summary

Dichlorotris(triphenylphosphine)ruthenium(II) catalyzes the hydrogen transfer from alcohols to olefins. Kinetic studies were carried out at 170—190°C using the ruthenium(II) complex as homogeneous catalyst, benzyl alcohol, diphenylcarbinol, methylphenylcarbinol and benzoin as the hydrogen donors, benzylideneacetone as the hydrogen acceptor, and dibenzyl ether as a solvent. The IR spectra and GLC were used to monitor the reaction and the isotope effects were determined in order to elucidate the role of the catalyst and the mechanism of hydrogen transfer. In the reaction mixture $RuCl_2(PPh_3)_3$ is converted by the alcohols into $RuH_2(CO)(PPh_3)_3$, which then hydrogenates benzylideneacetone. The kinetic data are compatible with the expression.

$$\text{reaction rate} = k_{obs}[\text{Ru}][\text{olefin}][\text{alcohol}]$$

The rate-determining step of this reaction is considered to be the transfer of hydrogen from the alcohol to a ruthenium species.

Introduction

Catalytic hydrogen transfer from organic compounds to olefins, called transfer hydrogenation, has some advantages over hydrogenation by molecular hydrogen. Both heterogeneous and homogeneous catalyst systems have been reported to be suited for the reaction [1]. Methyl linoleate or soybean oil can be hydrogenated to monoenes selectively under nitrogen in the presence of $PtCl_2(PPh_3)_2/SnCl_2$ [2], $PtCl_2(AsPh_3)_2/SnCl_2$ [2], $PdCl_2(PPh_3)_2$·[3] or NiX_2-$(PPh_3)_2$ (X = Cl, Br and I) [4] in a benzene/methanol solution. $Fe(CO)_5$ [5], $CoH_3(PPh_3)_3$ [6], $RhCl(CO)(PPh_3)_2$ [7], $RuCl_2(C_5H_5N)_4$ [8], $RuCl_2(PPh_3)_3$ [9—13], $IrHCl_2(Me_2SO)_3$ [9,14—16] and $IrBr(CO)(PPh_3)_2$ [9] have been reported to catalyze the hydrogen transfer from alcohols to olefins and ketones. These reactions require rather drastic conditions and only one detailed study of their mechanism, with $RhH(PPh_3)_4$ as catalyst, seems to have been reported [7]. $RuCl_2(PPh_3)_3$ is the most widely used catalyst for homogeneous hydrogen transfer reactions. This study was undertaken to elucidate the mechanism of the hydrogen transfer from alcohols to α,β-unsaturated carbonyl compounds and the role of $RuCl_2(PPh_3)_3$ as catalyst in this reaction.

Results and discussion

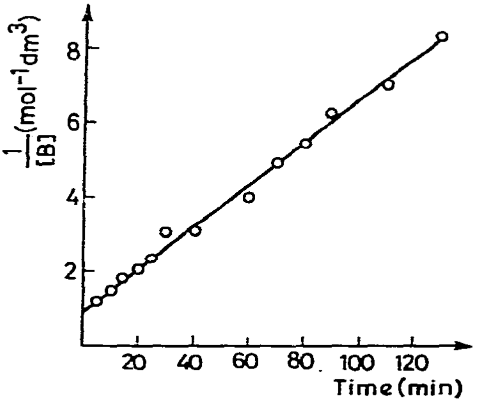
The kinetic experiments were carried out in dibenzyl ether at temperatures between 170 and 190°C. Equimolar amounts of benzylideneacetone (B_0) and benzyl alcohol (A_0) were used in the presence of a small amount of $RuCl_2(PPh_3)_3$ and the reactions were followed by GLC until 70—90% of the starting materials had reacted. A typical run can be seen in Fig. 1, in which 1/[B] vs. plotted the time, $[B]_0$ being the initial concentration of benzylideneacetone and benzyl alcohol ($[A]_0 = [B]_0$) and [B] the actual concentration of both reactants. The straight line obtained indicates that the total order of the reaction is two. This is consistent (inter alia) with eq. 1.

$$-\frac{d[A]}{dt} = k_{obs}[A][B] \qquad (1)$$

Integration of eq. 1 gives eq. 2.

$$\log\frac{[B]}{[A]} = \log\frac{[B]}{[A]_0} + ([B]_0 - [A]_0)\frac{k_{obs}}{2.30}\,t \qquad (2)$$

where [A] and [B] are the actual concentrations at time t [17]. A plot of log[B]/[A] against t will be a straight line if the rate of reaction can be expressed by eq. 1. This was found to be case (Fig. 2), which means that the reaction is first order with respect to both reactants A and B.



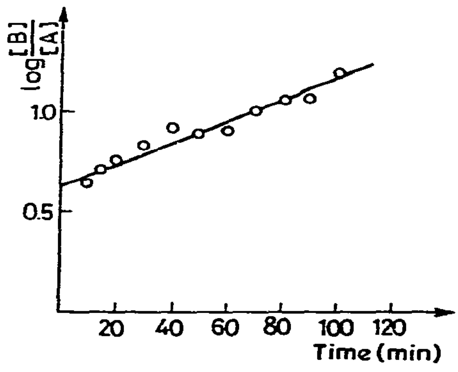


Fig. 1. Plot of the reciprocal concentration of benzylideneacetone [B] (benzyl alcohol) vs. time. 3.46 × 10^{-3} M $RuCl_2(PPh_3)_3$, 1.1 M benzylideneacetone, and 1.1 M benzyl alcohol in dibenzyl ether; reaction temperature 190°C, total volume: 4 ml.

Fig. 2. Plot of log[A]/[B] vs. reaction time. 9.23 × 10^{-4} M $RuCl_2(PPh_3)_3$, 1.28 M benzyl alcohol, 0.456 M benzylideneacetone in dibenzyl ether; reaction temperature 190°C, total volume: 4 ml.

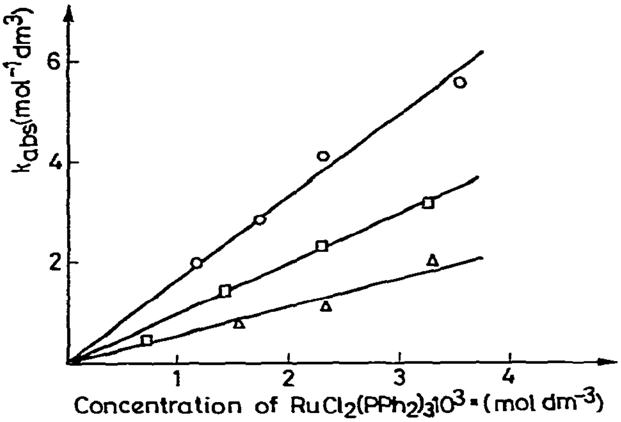


Fig. 3. Dependence of rate of transfer-hydrogenation of benzylideneacetone on catalyst concentration in dibenzyl ether at 170 (△), 180 (□) and at 190°C (○) by 1.1 *M* benzyl alcohol and 1.1 *M* benzylideneacetone.

When the runs are carried out with equal concentrations of benzylideneacetone and benzyl alcohol ($[B]_0 = [A]_0$) and different amounts of the catalyst a straight line is obtained in plotting the rate against the catalyst concentration (Fig. 3) i.e., there is a first order dependence on the catalyst.

Reactions involving the presence of an excess of free triphenylphosphine (ratios of 10 or 50 of free added phosphine to catalyst) had the same rate.

The rate with $PhCH_2OD$ as the donor molecule was significantly lower. The ratio k_H/k_D was found to be 2.5, representing a marked primary kinetic isotope effect. The theoretical value for the kinetic isotope effect calculated from the stretching frequencies ν(OH) 3605.7 cm^{-1} and ν(OD) 2773.7 cm^{-1} of the benzyl alcohol was found to be 3.63 [18]. A much smaller effect (k_H/k_D = 1.33) was reported for the hydrogen transfer reaction from 2-propanol to cycloheptene catalysed by $RhH(PPh_3)_4$ [7].

From reactions at various temperatures the following activation parameters were calculated (using k_{obs} values tabulated in Table 1): $\Delta E_a = 92.1$ kJ mol^{-1}, $\Delta H^{\ddagger} = 88.4$ kJ mol^{-1}, $\Delta S^{\ddagger} = 79$ kJ mol^{-1} K^{-1}.

TABLE 1

THE RATE CONSTANT k_{obs} FOR SEVERAL HYDROGEN DONOR SUBSTRATES

Substrate	k_{obs} × 10 (mol^{-2} l^2 s^{-1})	Temperature (°C)
Benzyl alcohol	0.93	170
	1.67	180
	2.75	190
Benzyl alcohol (D_1)	1.09	190
Diphenylcarbinol	0.62	190
Methylphenylcarbinol	0.83	190
Benzoin	0.15	190
Benzyl alcohol [a]	2.70	190

[a] Catalyst $RuH_2(CO)(PPh_3)_3$.

Several primary and secondary alcohols were investigated as hydrogen donors and found to form stoichiometric amounts of aldehydes and ketones, respectively. The results of the kinetic experiments are summarized in Table 1. This shows that benzyl alcohol has the highest ability to supply hydrogen.

The aldehydes and ketones formed from the hydrogen-donor alcohols during the transfer reaction did not retard the reaction as can be seen from Figs. 1 and 2. In all the catalytic hydrogen transfer experiments the reaction order did not change for up to 90% conversions. This suggests that the carbonyl compounds formed do not compete with other reaction partners for coordination sites on the metal complex.

$RuCl_2(PPh_3)_3$ reacts with benzyl alcohol, albeit slowly, even at room temperature. A small amount of the complex suspended in benzyl alcohol and dibenzyl ether produced an orange colour of the mixture after 0.5 h. The same reaction proceeded faster at 60° C and an intense red colour, characteristic for $RuHCl(PPh_3)_3$ developed. Unfortunately, the very weak ν(RuH) absorption band in $RuHCl(PPh_3)_3$ could not be detected [19]. However, another peak at 1710 cm^{-1} appeared gradually and this absorption was attributed to the carbonyl group of benzaldehyde. The benzaldehyde formed was determined quantitatively by GLC.

No decarbonylation of the benzaldehyde was observed at 60° C during 10 h. On introducing maleic acid diethyl ester to the mixture mentioned above isomerization to diethyl fumarate and hydrogenation to diethyl succinate occurred. Identical results were obtained using $RuHCl(PPh_3)_3$ prepared by a known procedure [19], but $RuCl_2(PPh_3)_3$ was inactive. On raising the tempera-

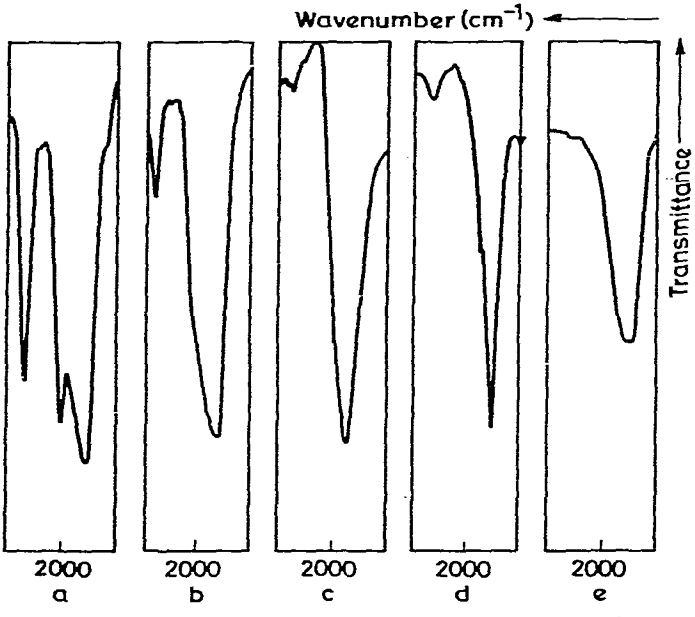


Fig. 4. a) The IR spectrum of the reaction mixture of benzyl alcohol and $RuCl_2(PPh_3)_3$ in dibenzyl ether at 190° C. b) The IR spectrum of the reaction mixture after 0.5 h. c) The IR spectrum (in Nujol) of the residue from the reaction mixture. d) The IR spectrum of the product isolated from the reaction mixture. e) The IR spectrum of $RuCl_2(PPh_3)_3$, benzyl alcohol, and benzylideneacetone after 50 min at 200° C.

ture above 120°C the intense purple red colour of the mixture turned to yellow. After reaching the reaction temperature (190°C) the IR spectrum of the solution showed bands at 2060, 1995 and 1950 cm^{-1} (Fig. 4a). The intensity of the two absorption bands at higher wave numbers diminished during the reaction, as can be seen in Fig. 4b, and after two hours only the broad absorption band around 1950 cm^{-1} remained. Evaporation of the solvent and the liquid components left a residue which showed a strong absorption band at 1960 cm^{-1} in Nujol (Fig. 4c). The same IR features of the reaction mixture were found also when other hydrogen-donating substrates such as benzoin or diphenylcarbinol were used.

In an attempt to isolate the most stable species in the catalytic cycle we treated $RuCl_2(PPh_3)_3$ with benzyl alcohol in dibenzyl ether at 190—200°C for 45 min. Diethyl ether was added to the cooled solution and pale yellow crystals of $RuH_2(CO)(PPh_3)_3$ separated (see Fig. 4d)[20].

$RuCl_2(PPh_3)_3$ dissolves in freshly distilled benzaldehyde and dibenzyl ether at room temperature, and a red colour develops owing to formation of $[RuCl_2(PPh_3)_2]_2$ [21], which was isolated as nice red prisms. On heating the mixture at 100°C for 10 min the red colour was maintained and no formation of ruthenium carbonyl complexes could be detected by IR. When the temperature was raised to 200°C the red colour turned to yellow in a few minutes and two medium absorption bands at 2062 and 2001 cm^{-1} appeared in the IR spectrum. These absorption bands could be assigned to the $\nu(CO)$ frequences of *cis*-$RuCl_2(CO)_2(PPh_3)_2$ [22]. GLC analysis of the mixture showed the presence of benzene formed through decarbonylation of benzaldehyde by $RuCl_2(PPh_3)_3$.

Heating a mixture of $RuCl_2(PPh_3)_3$ with an excess of benzylidenacetone and benzyl alcohol in dibenzyl ether to 100°C for 10 min gave a red colour and no

SCHEME 1

THE FORMATION OF VARIOUS RUTHENIUM COMPLEXES FROM $RuCl_2(PPh_3)_3$ DURING THE HYDROGEN TRANSFER REACTION

$$RuCl_2(PPh_3)_3 + PhCH_2OH \rightarrow \begin{array}{c} Ru(OCH_2Ph)Cl(PPh_3)_3 + HCl \\ \downarrow \\ RuClH(PPh_3)_3 + PhCHO \end{array} \quad (3)$$

$$RuHCl(PPh_3)_3 + PhCH_2OH \rightarrow \begin{array}{c} Ru(OCH_2Ph)H(PPh_3)_3 + HCl \\ \downarrow \\ RuH_2(PPh_3)_3 + PhCHO \end{array} \quad (4)$$

$$RuH_2(PPh_3)_3 + PhCHO \rightarrow RuH_2(CO)(PPh_3)_3 + PhH \quad (5)$$

$$RuCl_2(PPh_3)_3 + PhCHO \rightarrow RuCl_2(CO)(PPh_3)_3 + PhH \quad (6)$$

$$RuCl_2(CO)(PPh_3)_3 + PhCHO \rightarrow RuCl_2(CO)_2(PPh_3)_2 + PhH + PPh_3 \quad (7)$$

$$\left.\begin{array}{l} RuCl_2(CO)(PPh_3)_3 \\ \quad \text{or} \\ RuCl_2(CO)_2(PPh_3)_2 \end{array}\right\} + 2\ PhCH_2OH \rightarrow RuH_2(CO)(PPh_3)_3 + 2\ PhCHO \quad (8)$$

absorptions were found in the IR region between 2200 and 1800 cm^{-1}. When the mixture was kept at 200°C for 10 min the IR spectrum was the same as that in Fig. 4a. After further heating at this temperature for 40 min only one broad absorption band at 1957 cm^{-1} could be seen in the IR (Fig. 4e).

On the basis of the above results the reaction sequence shown in Scheme 1 is suggested for the reaction of $RuCl_2(PPh_3)_3$ with hydrogen donor molecules to give the catalytically active species of the hydrogen transfer process.

Even at low temperatures (50°C) the O—H bond of the donor undergoes oxidative addition to $RuCl_2(PPh_3)_3$, and this is followed by reductive elimination of HCl promoted by the ether solvent. β-H elimination from the benzyloxy complex then gives $RuHCl(PPh_3)_3$ and benzaldehyde. Above 120°C, in a similar reaction, the second chlorine atom of the ruthenium complex is removed again giving benzaldehyde and hydrogen chloride, and $RuH_2(PPh_3)_3$ is formed according to eq. 4. On raising the temperature still further the aldehyde is decarbonylated both by $RuH_2(PPh_3)_3$ and $RuCl_2(PPh_3)_3$ (possibly present) according to eqs. 5, 6 and 7, and the corresponding ruthenium carbonyl complexes, *cis*-$RuCl_2(CO)_2(PPh_3)_2$ and $RuH_2(CO)(PPh_3)_3$ are formed.

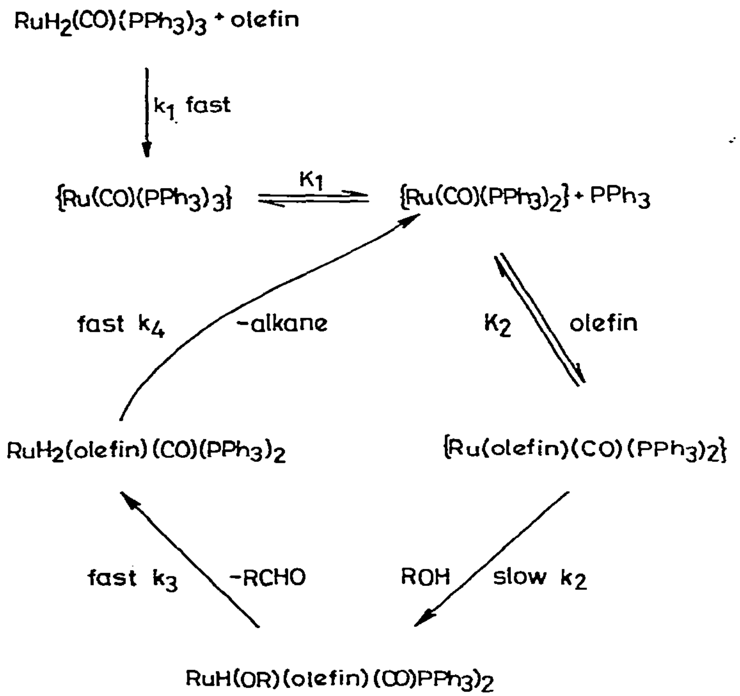
Upon reaching the actual reaction temperature (170—190 °C) the simple IR spectrum indicates that many of the intermediate ruthenium species have been converted into a single species in which most of the ruthenium is present, and this compound is responsible for the catalytic activity. This species was first assumed to be $RuH_2(CO)(PPh_3)_3$ formed by reaction 8 and isolated from the reaction mixture containing no olefin as described previously. However, the IR spectrum of this complex in dibenzyl ether is similar, but not identical to that of the reaction mixture. $RuH_2(CO)(PPh_3)_3$ reacts with benzylideneacetone to shift the ν(CO) to higher frequencies but no products could be isolated. In the reaction of this mixture with dihydrogen no change in the CO region of the spectrum was observed.

On the basis of the discussion above we assume that the $RuCl_2(PPh_3)_3$ first gives $RhH_2(CO)(PPh_3)_3$, and that this species starts the catalytic cycle. Kinetic experiments carried out under identical conditions with $RuH_2(CO)(PPh_3)_3$ and $RuCl_2(PPh_3)_3$ as catalysts gave the same reaction rates. Preliminary experiments with $RuH_2(CO)(PPh_3)_3$ as catalyst have shown that hydrogenation of olefins with H_2 proceeds much faster than the transfer hydrogenation reaction [23].

The kinetic data reported here can be interpreted in terms of Scheme 2. The $RuH_2(CO)(PPh_3)_3$ formed in the reaction mixture hydrogenates the olefin in a fast stoichiometric reaction (k_1), and the ruthenium compound $\{Ru(CO)(PPh_3)_3\}$ is formed. This is not necessarily a ruthenium(0) complex but more likely an orthometallated ruthenium(II) species. Similar suggestions were made for reactions of $RuH_2(PPh_3)_4$ and $RuH_4(PPh_3)_4$ with olefins recently [24]. We assume that one phosphine ligand of $\{Ru(CO)(PPh_3)_3\}$ dissociates almost totally under the reaction conditions (i.e. K_1 large, as indicated by the phosphine inhibition experiments) giving $\{Ru(CO)(PPh_3)_2\}$ in which form the catalyst is mainly present. This coordinatively unsaturated ruthenium species reacts with the olefin in a reversible reaction and $Ru(CO)(olefin)(PPh_3)_2$ which is only present in a very small concentration (K_2 small) is formed. This complex undergoes oxidative addition (k_2) with the alcohol in a slow, rate determining step giving the mixed hydrido alcoholato ruthenium complex, and this in a fast and irreversible

SCHEME 2

PROPOSED MECHANISM OF TRANSFER-HYDROGENATION FROM ALCOHOLS TO BENZYLIDENEACETONE CATALYSED BY $RuCl_2(PPh_3)_3$



β-H elimination reaction (k_3) yields the dihydrido ruthenium complex and the corresponding carbonyl compound. In this olefin-containing dihydridoruthenium(II) complex the olefin is intramolecularly hydrogenated (k_4) to give alkane, and the catalyst ends up as $\{Ru(CO)(PPh_3)_2\}$ in the catalytic cycle. Hydrogenation experiments of benzylideneacetone using $RuH_2(CO)(PPh_3)_3$ have shown k_2 to be much smaller than k_4 [22].

From Scheme 2 and the reasoning above the reaction rate can be expressed by eq. 9

$$r = -\frac{d[\text{olefin}]}{dt} = k_2\,[\text{ROH}][\text{Ru(olefin)(CO)(PPh}_3)_2] \tag{9}$$

Assuming k_1, k_3 and k_4 to be much larger than k_2 the amount of ruthenium catalyst present [Ru] is defined by eq. 10:

$$[\text{Ru}] = [\text{Ru(CO)(PPh}_3)_3] + [\text{Ru(CO)(PPh}_3)_2] + [\text{Ru(CO)(olefin)(PPh}_3)_2] \tag{10}$$

Incorporating the preequilibria 11 and 12

$$K_1 = \frac{[\text{Rh(CO)(PPh}_3)_2][\text{PPh}_3]}{[\text{Ru(CO)(PPh}_3)_3]} \tag{11}$$

$$K_2 = \frac{[\mathrm{Ru(CO)(olefin)(PPh_3)_2}]}{[\mathrm{olefin}][\mathrm{Ru(CO)(PPh_3)_2}]} \tag{12}$$

and eq. 10 into eq. 9 the reaction rate expression takes the form:

$$r = \frac{k_2K_1K_2[\mathrm{Ru}][\mathrm{olefin}][\mathrm{ROH}]}{[\mathrm{PPh_3}] + K_1 + K_1K_2[\mathrm{olefin}]} \tag{13}$$

Since in the nominator of eq. 13 the term K_1K_2 [olefin] is much smaller than K_1 (assuming $K_2 << K_1$) and $[\mathrm{PPh_3}] << K_1$, based on eq. 11, the simplified rate expression (eq. 14) is in good agreement with the experimental results. This suggests that in hydrogen transfer reactions the oxidative addition of the O—H bond of alcohols to a ruthenium complex is rate determining, and it is this step which requires more drastic conditions that the related reaction of the H—H bond.

$$r = k_2K_2[\mathrm{Ru}][\mathrm{olefin}][\mathrm{ROH}] \tag{14}$$

Experimental

Spectra were recorded on the following instruments: IR Carl Zeiss, Jena, UR-20; Mass spectra, Varian MAT 111 GS/115. The GLC analyses were carried out on a Carlo Erba Fractovap Model C chromatograph.

Catalysts

$\mathrm{RuCl_2(PPh_3)_3}$ [22], $\mathrm{RuHCl(PPh_3)_3}$ [19], $\mathrm{RuHCl(CO)(PPh_3)_3}$ [25] and $\mathrm{RuH_2(CO)(PPh_3)_3}$ [20] were prepared by standard procedures and were used without recrystallization.

Reagents

Reagent grade dibenzyl ether was dried over magnesium sulfate and distilled under nitrogen. Benzylideneacetone, benzoin (Koch-Light Ltd.) were used without purification. Benzhydrol and phenylmethylcarbinol (Koch-Light Ltd.) were dried over magnesium sulfate and distilled under nitrogen. $\mathrm{PhCH_2OD}$ was prepared from $\mathrm{PhCH_2OH}$ stirred with $\mathrm{D_2O}$ for several hours, separated from water, dried over magnesium sulfate and distilled under nitrogen. The $\mathrm{PhCH_2OD}$ was of IR purity, >95%. The catalysts, reagents, and solvent were stored under nitrogen in Schlenk-tubes. All nitrogen used was passed through a hot copper furnace to remove traces of oxygen.

Catalytic experiments

The reaction vessel was connected to a vacuum line system. The reaction vessel was a 10 ml Schlenk tube with a magnetic stirrer, stopcock and had a short neck sealed with a self-sealing serum cap through which samples were withdrawn by syringe, and it was connected to a nitrogen supply and vacuum. The appropriate amount of solid catalyst and benzylideneacetone were placed in the flask which was then evacuated. Dibenzyl ether and the appropriate alcohol were added from a syringe through the serum cap. The catalyst was dissolved and the vessel containing the orange coloured solution was placed in a thermostat bath. Since the reactions were carried out at more evaluated temperatures (between 170—190° C), time was allowed for the mixture to reach the reaction temperatures; five minutes usually sufficed. The samples of ca. 0.1—0.2 ml were removed by syringe, stored at 20° C, and analysed by GLC. For the separation of benzhydrol, benzylidineacetone, benzaldehyde and benzyl acetone, a 3 m polyethylene glycol column at 180° C was used.

The isolation of $RuH_2(CO)(PPh_3)_3$ from the reaction of $RuCl_2(PPh_3)_3$ with benzyl alcohol

A solution of 57 mg (0.06 mmol) $RuCl_2(PPh_3)_3$ and 0.3 ml benzyl alcohol in 1.3 ml dibenzyl ether was heated at 190° C for 45 min. The yellow solution was cooled to room temperature and kept for several days: small amounts of diethyl ether being added from time to time. Pale yellow crystals separated. IR spectrum in Nujol: ν(CO) 1937.9s; ν(RuH) 1900w, 1960.7s cm^{-1}; identical with reported data [19].

The reaction of $RuCl_2(PPh_3)_3$ with benzaldehyde in dibenzyl ether

A solution of 20 mg (0.021 mmol) $RuCl_2(PPh_3)_3$ and 0.1 ml benzaldehyde in 1.0 ml dibenzyl ether was heated at 100° C for 10 min. No absorption bands in the CO region were seen in the IR spectrum of the purple coloured mixture. The temperature was raised to 200° C and after 10 min the colour changed to yellow and strong absorption bands at 2000 and 2061 cm^{-1} appeared in the IR spectrum (identical with the spectrum of *cis*-$RuCl_2(CO)_2(PPh_3)_3$ prepared by the known procedure [22]).

Isomerization and hydrogenation of diethyl maleate by $RuHCl(PPh_3)_3$ formed in the reaction of $RuCl_2(PPh_3)_3$ with benzyl alcohol

A solution of 15 mg (0.016 mmol) $RuCl_2(PPh_3)_3$ and 1 ml (6.18 mmol) diethyl maleate and 3 ml (29.13 mmol) benzyl alcohol was heated at 60° C for 3 h. GLC analysis of the mixture (50 m capillary column, polyethylene glycol, 150° C) showed it to contain 40% diethyl maleate, 47% diethyl fumarate and 13% diethyl succinate.

The reaction of $RuCl_2(PPh_3)_3$ with benzaldehyde

A solution of 96 mg (0.1 mmol) $RuCl_2(PPh_3)_3$ in 2 ml benzaldehyde (freshly distilled and dried over Na_2SO_4) in a Schlenk tube was kept for 10 days under nitrogen. Deep red crystals deposited, and these were filtered off and shown to be $Ru_2Cl_4(PPh_3)_4$, 42 mg (30%). Anal. Found.: C, 61.99; H, 4.25 calcd. for $C_{72}H_{60}P_4Ru_2Cl_4$ (1392.12): C, 62.07; H, 4.34% [21].

The decarbonylation of benzaldehyde by $RuCl_2(PPh_3)_3$ giving cis-$RuCl_2(CO)_2(PPh_3)_2$

A solution of 20 mg (0.021 mmol) $RuCl_2(PPh_3)_3$ and 0.1 ml (0.97 mmol) benzaldehyde in 1.0 ml dibenzyl ether were heated at 100° C for 10 min. The intense purple-red solution showed no IR absorption in the ν(CO) region. When the mixture was kept at 200° C for 15 min the colour turned to yellow. The IR spectrum of the mixture showed intense absorption bands at 2001 and 2062 cm^{-1} which were identified as the ν(CO) frequencies of *cis*-$RuCl_2(CO)_2(PPh_3)_2$ by comparison with an authentic sample [22].

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