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Kinetics and mechanism of H_2-hydrogenation of styrene catalyzed by $[RuCl(dppb)(\mu\text{-}Cl)]_2$ (dppb = 1,4-bis(diphenylphosphino)butane). Evidence for hydrogen transfer from a dinuclear molecular hydrogen species ☆

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Abstract

Kinetic studies on the H_2-hydrogenation of styrene catalyzed by $[RuCl(dppb)(\mu\text{-}Cl)]_2$ (dppb = $Ph_2P(CH_2)_4PPh_2$) in N,N-dimethylacetamide solution, near ambient conditions have revealed a first-order dependence on Ru, and dependences on H_2 and on styrene that are first-order at lower concentrations and decrease with increasing concentration. Considered along with NMR and tensiometric data, the findings are interpreted in terms of a basic hydride route in which an initially formed, dinuclear, molecular hydrogen complex $(\eta^2\text{-}H_2)Ru(dppb)(\mu\text{-}Cl)_3RuCl(dppb)$ transfers both hydrogens to the styrene.

Keywords: Hydrogenation; Styrene; Ruthenium; Catalysis; Dihydrogen; Kinetics

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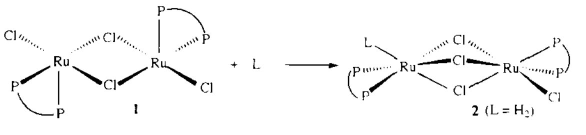
1. Introduction

Ruthenium complexes containing one chelating bis(tertiary phosphine) ligand per metal atom are key species for catalytic homogeneous hydrogenation reactions, and spectacular success of such ‘Ru(P–P)’ complexes in asymmetric hydrogenation of certain olefins, ketones and imines (when P–P is a chiral phosphine) has been demonstrated [1–3]. Kinetic and mechanistic studies on Ru(P–P) hydrogenation systems have been limited [4–6]. The most thorough one concerned hydrogenation of α,β-unsaturated carboxylic acids catalyzed by $Ru(binap)(O_2CMe)_2$ in MeOH [6]; this system operates via a previously well-established “unsaturate” route for Ru(II) species in which a Ru(II) (substrate) complex reacts with H_2 in the rate-determining step with resulting heterolytic cleavage of the H_2 to give a monohydride [6]. Following our discovery of reaction (1) for L = H_2 and other ligands (P–P = dppb, $Ph_2P(CH_2)_4PPh_2$), and our finding that complex **1** effectively catalyzes H_2-hydrogenation of alkenes [7] and imines [8] and transfer-hydrogenation (from propan-2-ol) of acetophenone [7], we decided to study in more detail the catalyzed H_2-hydrogenation of styrene and investigate the possible role of the $\eta^2\text{-}H_2$ species **2** in the reaction. This paper presents the results of kinetic studies on the catalytic hydrogenation, and shows that the data are consistent with transfer of the $\eta^2\text{-}H_2$ to styrene.



(1)

2. Experimental details

All synthetic reactions were carried out using standard Schlenk techniques. Solvents were generally dried over appropriate drying agents, distilled under N_2, and degassed prior to use. *N,N*-Dimethylacetamide (DMA) was stirred with CaH_2 for at least 24 h, vacuum distilled at 35–40°C, and stored under Ar in the dark. Purified Ar and N_2 (Union Carbide Canada Ltd.) were

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☆ Dedicated to Professor Fausto Calderazzo on the occasion of his 65th birthday, and for 25 years of close friendship.

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used without further purification. Hydrogen (Union Carbide Canada Ltd.) was passed through an Engelhard Deoxo catalytic hydrogen purifier to remove traces of oxygen; D_2 was used as received from Merck Frosst Canada Ltd. Reagent-grade PPh_3 and dppb, both from Strem Chem., were used as supplied. Styrene (Aldrich) was purified prior to use by passage through a column of activated alumina (Fisher, A-950 neutral chromatographic grade, 80–200 mesh). The primary ruthenium source was $RuCl_3 \cdot 3H_2O$ (approximately 42% Ru) obtained from Johnson Matthey Ltd., or Colonial Metals, Inc. Complex **1**, $[RuCl(dppb)(\mu\text{-}Cl)]_2$, was prepared by H_2-reduction of $[RuCl(dppb)]_2(\mu - Cl)_3$ as described previously [2], the latter mixed-valence complex being made by treatment of $RuCl_3(PPh_3)_2(DMA)$ with dppb [9].

The ^1H, $^{31}P\{^1H\}$ and ^2H NMR spectra (t = triplet, q = quartet) were recorded at room temperature on a Varian XL-300 (300 MHz for ^1H, 121.42 MHz for ^{31}P, 46.0 MHz for ^2H) FT-NMR spectrometer, the ^{31}P NMR shifts being reported relative to 85% H_3PO_4, with downfield shifts as positive.

Gas uptakes for stoichiometric or kinetic studies, and hydrogen solubility measurements in DMA solvent, were performed at a constant temperature (30°C) on a conventional constant pressure apparatus; the apparatus and general procedures employed have been described elsewhere [10]. The rates of styrene hydrogenation catalyzed by **1** were measured at concentrations of **1**, ranging from $(0.5\text{–}1.5) \times 10^{-3}$ M at various H_2-pressures (410–785 torr) and various substrate concentrations ([styrene] = 0.01–0.42 M), with only one parameter changed at a time.

3. Results and discussion

3.1. Styrene hydrogenation

DMA solutions of styrene absorb H_2 in the presence of catalytic amounts of **1**, and the rates at 30°C under H_2-pressures of approximately 1 atm are conveniently measurable. At the mM concentrations of catalyst used, complete conversion of styrene (at up to 0.42 mM) into ethylbenzene occurs, as evidenced by ^1H NMR spectroscopy (δ 1.03 t, $PhCH_2C\mathit{H}_3$; 2.40 q, $PhC\mathit{H}_2CH_3$) and the resonances caused by the styrene $-C\mathit{H}{=}C\mathit{H}_2$ protons at δ(6.9–5.3) disappear. At 1.5 mm Ru_2, under 1 atm H_2, conversion of 0.42 M styrene is complete within ca. 1 h. The corresponding reactions with D_2 give mainly a mixture of $PhCH(D)CH_2D$ and $PhCH(D)CHD_2$ as determined by ^1H, ^2H, and $^2H\{^1H\}$ NMR spectroscopy and mass spectrometry: the ^1H and ^2H spectra showed complex multiplets centred at δ 2.43 and δ 1.06, while the $^2H\{^1H\}$ spectrum showed singlets at the same positions because of $(-CH(\mathit{D}))$ and $(CH_2\mathit{D}$ and $-CH\mathit{D}_2)$, respectively. The relative integrations within each of the spectra suggest an approximately 1 : 1 mixture of the di- and tri-deuterated ethylbenzene, although the mass spectral data showed the presence of a small amount of $PhCH(D)CD_3$; no deuterium was incorporated into the phenyl group.

The catalyst precursor **1** can be recovered intact at the end of a catalytic run, as evidenced by the $^{31}P\{^1H\}$ NMR spectrum of the red-brown residue obtained by removing DMA and ethylbenzene under vacuum at 50°C; in C_6D_6, an AB quartet, $\delta_A = 64.0$, $\delta_B = 54.9$ ($^2J_{AB}$ 47.0 Hz) corresponds exactly to that of **1** [2]. The catalyst could be reused without loss of activity.

The H_2-solubility in DMA obeys Henry's Law at least up to 800 torr at 30°C, the plot of molar solubility vs. partial pressure of H_2 being linear with a Henry's Law Constant K_H ($= [H_2]/H_2$ pressure) of 2.32×10^{-6} M $torr^{-1}$. DMA was chosen as solvent because of its low vapor pressure (less than 3 torr at 30°C [11]), which is convenient for operation of the gas-uptake apparatus under O_2-free conditions (complex **1** is air-sensitive in solution), and because corrections needed to calculate the required partial pressure of H_2 (P_{H_2}) from the total measured pressure are negligible.

3.2. Rate measurements

A typical plot of H_2-uptake vs. time for the styrene hydrogenation is shown in Fig. 1. The 100–200 s "induction period" results from the time taken for **1** to dissolve in DMA (the complex is added from a small glass bucket to the solution after evacuating the vessel and establishing the H_2-atmosphere [10]); the subsequent maximum linear rates were readily measured, the extent of the linear region depending on the [styrene] (see below). The maximum rates at 30°C are summarized in Table 1.

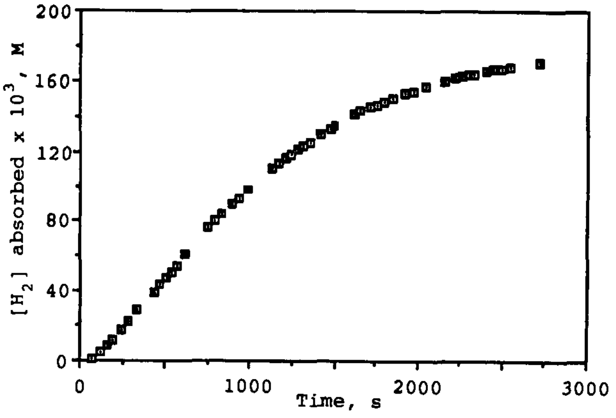


Fig. 1. A typical H_2-uptake plot for the hydrogenation of styrene catalyzed by **1** in DMA at 30°C and 785 torr H_2; [styrene] = 0.18 M; $[Ru_2]_{Total}$ = 0.80 mM; $[H_2]$ = 1.82 mM.

Table 1
Kinetic data for hydrogenation of styrene catalyzed by $[RuCl(dppb)(\mu\text{-}Cl)]_2$ in DMA at 30°C

$[Ru_2]_T$ mM	[styrene] × 10^2 M	P_{H_2} torr	$[H_2]$ mM	Max. Rate × 10^5 M s^{-1} [a]
1.52	41.5	785	1.82	20.5
1.03	41.5	785	1.82	12.7
0.80	41.5	785	1.82	11.1
0.50	41.5	785	1.82	6.57
0.80	18.0	785	1.82	10.6
0.80	4.30	785	1.82	4.84
0.80	3.70	785	1.82	4.00
0.80	2.40	785	1.82	3.10
0.80	1.80	785	1.82	2.53
0.80	1.80	785	1.82	2.49
0.80	0.90	785	1.82	1.39
0.80	4.30	685	1.59	4.11
0.80	4.30	590	1.37	3.93
0.80	4.30	500	1.16	3.57
0.80	4.30	410	0.95	3.13

[a] Error in rate values is estimated at ca. ±5%.

The dependence on $[Ru_2]$ at an initial [styrene] = 0.415 M under 785 torr H_2 (1.82 mM) is first-order (Fig. 2). The dependence on H_2 at 0.80 mM Ru_2 and 0.043 M styrene (Fig. 3) is first-order at lower $[H_2]$, tending to somewhat less than first-order with increasing $[H_2]$.

The dependence on initial substrate concentration at 0.80 mM Ru_2 and 1.82 mM H_2 goes from first- to zero-order with increasing [styrene] (Fig. 4); the uptake plots for the experiments at higher initial [styrene] show longer linear rates because of the zero-order dependence under these conditions, while the individual uptake plots at lower [styrene] (up to approximately 0.05 M) analyze for a first-order loss of styrene, after allowing for the "solubility-induction period".

3.3. Spectroscopic data

As noted above, **1** can be recovered unchanged after a catalytic hydrogenation. Examination of samples taken from the solution during the hydrogenation using $^{31}P\{^1H\}$-NMR spectroscopy reveals a two-AB pattern (δ 52.5, 51.2, ^2J = 43.5 Hz; δ 52.0, 49.9, ^2J = 40.2 Hz) and this is attributed to the triply chloride-bridged species **3** containing a single, terminal DMA ligand [2]; the identical spectrum is obtained on dissolving **1** in DMA, or on dissolving **1** in DMA containing a 50-fold excess of styrene. The spectrum is essentially the same as that recorded for **3** formed in situ in benzene or $CHCl_3$ solutions [2].

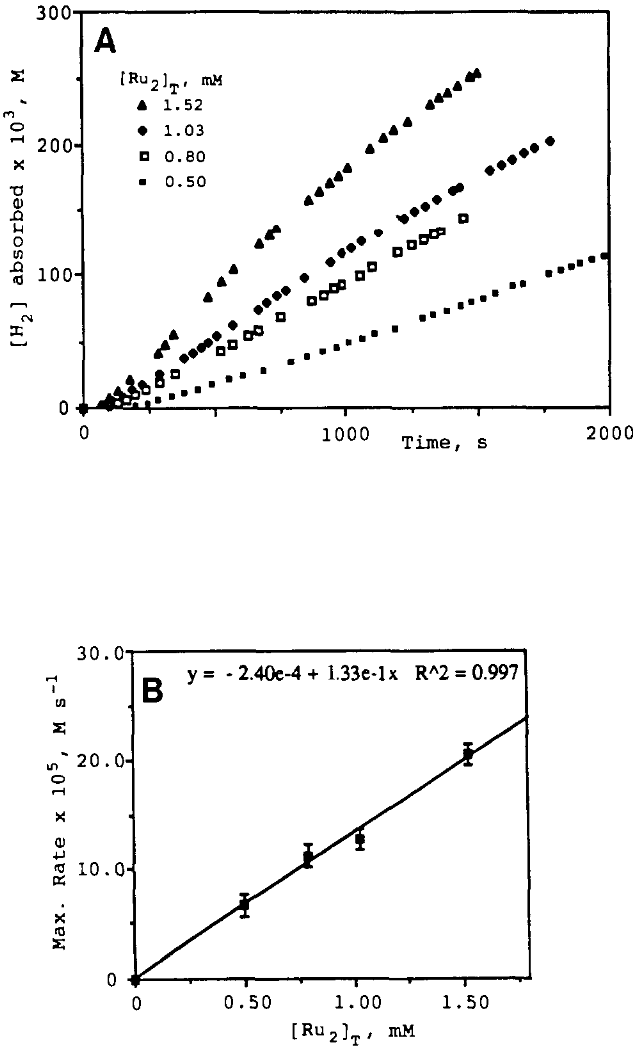


Fig. 2. (A) Rate plots for styrene hydrogenation catalyzed by **1** in DMA at 30°C, at various $[Ru_2]_{Total}$; [styrene] = 0.415 M; $[H_2]$ = 1.82 mM; (B) Dependence of the maximum hydrogenation rate on $[Ru_2]_{Total}$ (from data of A).

It should be noted during investigation of the samples that, because of the relatively high hydrogenation activity of **1** (typical turnovers for the solutions examined were about 10 min^{-1}), the dissolved H_2 was quickly depleted and could not be replinished; thus, the sampled solutions contained H_2 at low concentration and so consisted essentially of **1** and styrene (and ethylbenzene). The data thus reveal no evidence for

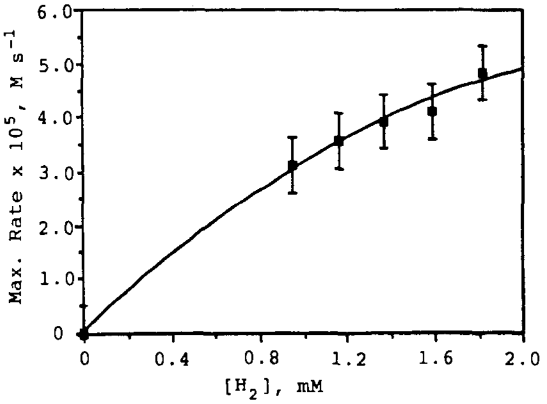


Fig. 3. Dependence of the maximum hydrogenation rate on $[H_2]$ at 30°C; $[Ru_2]_{Total}$ = 0.80 mM, [styrene] = 43 mM.

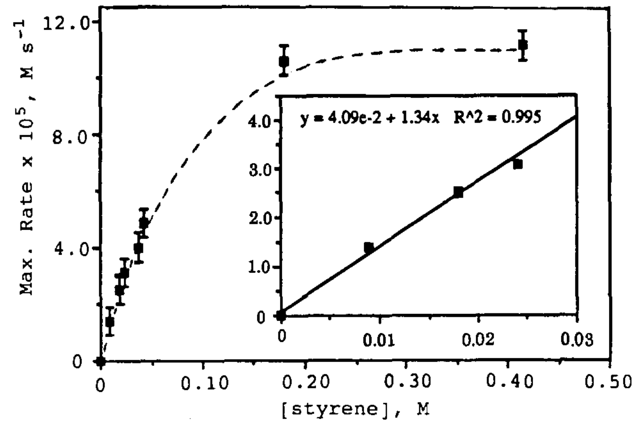
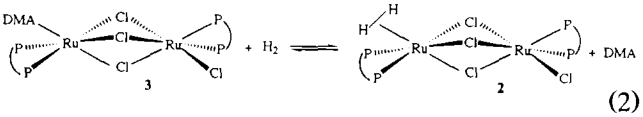


Fig. 4. Dependence of the maximum hydrogenation rate on [styrene] at 30°C; $[Ru_2]_{Total} = 0.80$ mM, $[H_2] = 1.82$ mM. The inset shows the initial portion of the rate plot expanded.

formation of a styrene adduct in DMA (e.g. as in Eq. (1) with L = styrene).

The existence of the equilibrium shown in Eq. (1) for $L = H_2$ was established experimentally in benzene and toluene solution [2,7]; for **2**, the η^2-H_2 is detected at δ-11.0 by ^{1}H NMR, and the $^{31}P\{^1H\}$ NMR spectrum shows the expected two-AB pattern (δ 53.7, 53.2, $^2J = 44.4$ Hz; δ 53.8, 38.3, $^2J = 33.8$ Hz), the latter one being assigned to the phosphorus atoms at the $Ru(H_2)$ moiety [2,7]. The corresponding H_2-equilibrium in DMA is that shown in Eq. (2), and this almost certainly exists, but the evidence is more equivocal. It is impossible to detect any high-field ^{1}H NMR signal in DMA solutions of **1** (i.e. comprised of **3**) under 1 atm H_2 even using solvent-suppression techniques; in the $^{31}P\{^1H\}$ spectrum, one new AB pattern is clearly seen (δ 54.5, 38.8, $^2J = 34.0$ Hz), while a doublet centred at δ 53.7 with $^2J = 42.9$ Hz is considered to be half of the second AB pattern, the other half being buried under the AB patterns of unreacted **3**. The $^{31}P\{^1H\}$ data are thus comparable to those assigned definitively to species **2** in benzene/toluene (see above). The conversion to the supposed η^2-H_2 species in DMA under 1 atm H_2 was variable, however, and depended on agitation of the NMR-tube, suggesting that the diffusion rates of H_2 from the gas phase to solution were a problem. Nevertheless, qualitatively in DMA there is a reaction with H_2, and the product appears to be dinuclear, and is presumably **2**.



(2)

In accord with the existence of reaction (2) in DMA, rapid, reversible H_2 uptakes of approximately 0.4 mol mol^{-1} of **1**(**3**) are observed for DMA solutions of **1** at 1 atm H_2 and 30°C. These data will be considered further, within the discussion and analysis of the kinetic data.

3.4. Analysis of the kinetic data

The first-order dependence on $[Ru]_T$ (where T = total), the first- to zero-order dependence on [styrene], and the generally fractional dependence on $[H_2]$, are most readily interpreted in terms of the following, overall basic "hydride" route involving the dinuclear, η^2-H_2 species **2**:

$$\mathbf{3} + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{2} + \text{DMA} \qquad (3)$$

$$\mathbf{2} + \text{styrene} \xrightarrow[\text{(DMA)}]{k_2} \mathbf{3} + \text{ethylbenzene} \qquad (4)$$

Although the DMA ligand plays a role in step (3) and possibly in step (4) (see below), the kinetic data reveal no information on these roles because the reaction is carried out in DMA. The spectroscopic data show that DMA is present as a terminal ligand on one Ru in the dinuclear species **3**, and that **2** is formed to some extent under H_2.

Application of the steady-state treatment for the intermediate **2** yields the rate law shown in Eq. (5).

$$\text{Rate} = -\frac{d[H_2]}{dt} = \frac{k_1 k_2 [Ru_2]_T [\text{styrene}][H_2]}{k'_{-1} + k_1[H_2] + k_2[\text{styrene}]} \qquad (5)$$

where $[Ru_2]_T = \mathbf{2} + \mathbf{3}$, and $k'_{-1} = k_{-1}$ [DMA]

At constant $[H_2]$ and constant [styrene], the rate Eq. (5) reduces to

Rate $= k_{obs}[Ru_2]_T$, where

$$k_{obs} = \frac{k_1 k_2 [\text{styrene}][H_2]}{k'_{-1} + k_1[H_2] + k_2[\text{styrene}]} \qquad (6)$$

The first-order dependence of the maximum rate on $[Ru_2]_T$ (Fig. 2B) is consistent with the analysis, the slope giving $k_{obs} = 0.13$ s^{-1}. The kinetic data alone do not distinguish between an active dinuclear Ru_2 or a fully formed mononuclear Ru catalyst, but the spectroscopic data reveal the presence of only dinuclear species, and thus the catalysis must proceed via such species; if highly active, non-detectable mononuclear species were the true catalysts, the kinetic order in $[Ru_2]_T$ would be 0.5, this being governed by some immeasurably small predissociation of the dinuclear to mononuclear species.

The dependence on [styrene] (Fig. 4) is in accord with Eq. (6) changing from first- to zero-order with increasing [styrene]; at [styrene] < 0.025 M, the plot of maximum rate vs. [styrene] is linear with slope $k_1 k_2 [Ru_2]_T [H_2]/(k'_{-1} + k_1[H_2])$, while at the highest

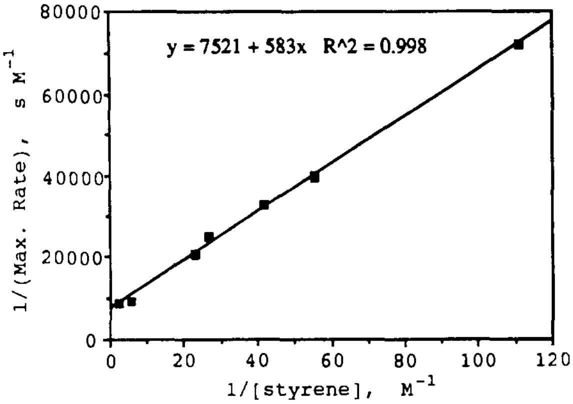


Fig. 5. Plot of (Rate)$^{-1}$ vs. ([styrene])$^{-1}$; $[Ru_2]_{Total}$ = 0.80 mM, $[H_2]$ = 1.82 mM, at 30°C.

[styrene] the rate becomes $k_1[Ru_2]_T[H_2]$. The standard analysis for such data makes use of a double reciprocal plot based on rearrangement of Eq. (6) to give:

$$\frac{1}{\text{Rate}} = \frac{k'_{-1} + k_1[H_2]}{k_1 k_2 [Ru_2]_T [H_2]} \cdot \frac{1}{[\text{styrene}]} + \frac{1}{k_1[Ru_2]_T[H_2]} \qquad (7)$$

At constant $[Ru_2]_T$ and $[H_2]$, the plot of 1/rate vs. 1/[styrene] should be linear; Fig. 5 shows such a plot, with slope 538 s and intercept 7521 s M^{-1}, and the k_1 value of 93 M^{-1} s^{-1} is obtained from the intercept for conditions when $[Ru_2]_T$ = 0.80 mM and $[H_2]$ = 1.82 mM at 30°C.

Eq. (6) also accounts for the observed dependence on $[H_2]$, which mirrors that for styrene except at the highest $[H_2]$ used (corresponding to 785 torr) the zero-order is not quite attained (Fig. 3). The data are again analyzed via a double reciprocal plot (1/rate vs. 1/$[H_2]$) according to Eq. (8) which is readily derived from Eq. (6). The plot (Fig. 6) yields a good straight

$$\frac{1}{\text{Rate}} = \frac{k'_{-1} + k_2[\text{styrene}]}{k_1 k_2 [Ru_2]_T [\text{styrene}]} \cdot \frac{1}{[H_2]} + \frac{1}{k_2[Ru_2]_T[\text{styrene}]} \qquad (8)$$

line with slope 20.9 s, and an intercept of 10130 s M^{-1} from which a k_2 value of 2.9 M^{-1} s^{-1} is obtained for $[Ru_2]_T$ = 0.80 mM and [styrene] = 43 mM at 30°C.

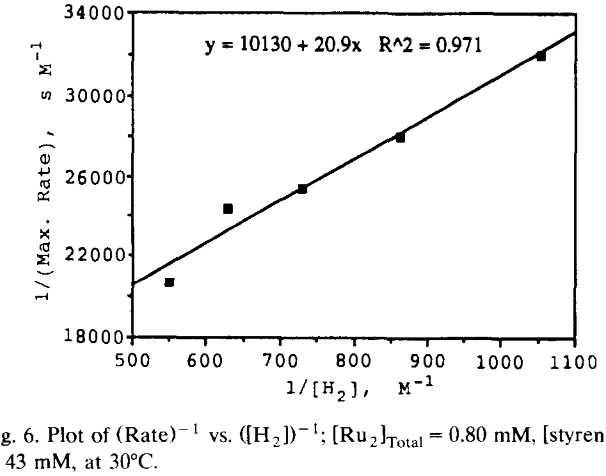


Fig. 6. Plot of (Rate)$^{-1}$ vs. ($[H_2]$)$^{-1}$; $[Ru_2]_{Total}$ = 0.80 mM, [styrene] = 43 mM, at 30°C.

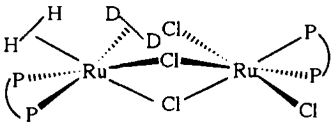
The values of k_1 (93 M^{-1} s^{-1}) and k_2 (2.9 M^{-1} s^{-1}) can be used to derive values of k'_{-1} from the slopes of Figs. 5 and 6 (see Eqs. (7) and (8)); the estimated values are 0.056 s^{-1} and 0.066 s^{-1}, respectively, at 30°C for the conditions specified earlier. The values, obtained from the styrene- and H_2-dependences, respectively, are in reasonable agreement, and show that the data are internally consistent.

3.5. Hydrogenation mechanism

Formation of the η^2-H_2 dinuclear species, followed by hydrogen transfer to styrene, Eqs. (3) and (4), accommodate well the kinetic data. The k_1 and k'_{-1} values at 30°C may be combined to reveal that in the absence of styrene reaction (3) would be established as an equilibrium within a few seconds, with an equilibrium constant (K) of 1500 ± 150 M^{-1}. We were unable to obtain reliable K values in DMA by NMR spectroscopy, but the H_2-uptake of approximately 0.4 mole/Ru_2 corresponds to a K value of approximately 370 M^{-1}. This value is considered to be a lower limit because in the experimental procedure used **1** is exposed to H_2 in the solid state prior to dissolution, and the possibility of some reaction with H_2 in the solid state [12] can not be ruled out. Thus, although the stoichiometrically measured K value is about four times smaller than the kinetically measured value, we consider that this is good agreement and offers strong support to the suggested mechanism. Noteworthy is that the K value for binding of H_2 to **1** in CH_2Cl_2 was determined as 1400 M^{-1} at 25°C using $^{31}P\{^1H\}$ NMR data, and the corresponding k_1 value was measured by stopped-flow data as 24 M^{-1} s^{-1} [13]; the agreement with the kinetically determined values in DMA is remarkable and perhaps fortuitious, but it offers further indirect support for the supposed mechanism. The propensity of the chloro(phosphine) ruthenium(II) moiety to bind η^2-H_2 is well demonstrated by the existence of equilibrium (2), in that H_2 at approximately 1 mM competes successfully with neat DMA (approximately 10.8 M) for a coordination site, and DMA is a reasonably strong donor ligand with a donor number close to that of, for example, dimethylsulfoxide [14].

Hydrogen transfer from an η^2-H_2 moiety is not widely documented. The catalytic activity of a molecular hydrogen complex more commonly results from creation of a vacant coordination site by loss of the labile η^2-H_2 [15]; however, catalytic hydrogenation of alkynes to alkenes using an iron η^2-H_2 complex is thought to involve intramolecular transfer from the η^2-H_2 to a σ-vinyl ligand [16], and work in our laboratory demonstrated the occurrence of stoichiometric hydrogen transfer from another binuclear ruthenium η^2-H_2 complex [17].

The details of the hydrogen-transfer step(s) in reaction (4) remain, of course, obscure. Complex **1** does catalyze H_2/D_2 exchange [7] and we think that, as suggested by others [18,19], the exchange could take place via intermediates such as **4**, in which the dinuclearity is maintained and a vacant site is generated when one of the bridging chlorides becomes terminal. Involvement of mononuclear species such as **5**, analogous to the known $Ru(H)_2(PR_3)_2(H_2)_2$ complexes [20], seems unlikely because the dinuclear structure of **1** is maintained even in the presence of an excess of a ligand such as amine, nitrile and DMA [2]. If one of the H_2/D_2 molecules were replaced by a π-bonded alkene, plausible hydrogen transfers to effect reaction (4) via standard organometallic pathways [21] can be readily envisaged. The detection of some $PhCH(D)CHD_2$ in the deuteration experiments is consistent with the process shown in Eq. (9); a reversible first step (hydrometallation, and the reverse β-hydride elimination), coupled with the demonstrated



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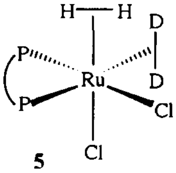

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$$(H)_2Ru(PhCH{=}CH_2) \rightleftharpoons (H)Ru{-}CH(Ph){-}CH_3 \longrightarrow \underset{\mathbf{3}}{Ru} + PhCH_2CH_3 \qquad (9)$$

H_2/D_2 exchange, allows for incorporation of more than one D atom at the β-carbon of ethylbenzene. An entering DMA ligand, needed to regenerate **3**, could assist the hydrogen transfer, and indirect evidence for this is provided by the observation of much lower catalytic activity in benzene solution under corresponding conditions (by a factor of approximately 10). The 1,2-dideuteroethylbenzene product could result from the process shown in Eq. (9) but a contributing pathway involving direct hydrogen transfer to *non-coordinated* styrene cannot be ruled out. This could involve stepwise H-atom transfers via styryl radical intermediates, and this has been demonstrated for hydrogenation of α-methylstyrene with $MnH(CO)_5$ as catalyst [22], while a direct two H-atom transfer from a postulated dihydrido species $Cr(H)_2(CO)_4$ to a non-coordinated diene has been invoked to rationalize some deuterium-tracer studies [23,24], but more recent studies on chromium carbonyl systems [18] suggest that any "dihydrido" species is more likely to have been an η^2-H_2 species. Even more relevant is the documented pairwise transfer of H_2 from $Ru(\eta^2\text{-}H_2)(H)_2(PPh_3)_3$ to styrene, demonstrated by the PHIP technique (*para*-hydrogen induced polarization) [25], for which our dppb catalyst would be a good candidate.

There is no evidence in the present study that the DMA plays the role of a basic ligand in promoting heterolytic cleavage of H_2 (for example, Eq. (10)). Such a role for DMA is well documented for dichlororuthenium(II) complexes containing monodentate tertiary phosphines [21], although stronger bases appear to be required for corresponding chelated ditertiary phosphine species [2,26]; indeed, **1** is isolated from H_2-reduction of $Ru_2Cl_5(dppb)_2$ in DMA [2], and no monohydride species are formed, although $[Ru(H)Cl(dppb)]_3$ may be formed subsequently by H_2-reduction in the presence of NEt_3 [26]. The lack of formation of monohydrides (reportedly a key step in hydrogenations catalyzed by $Ru(binap)(O_2\text{-}CMe)_2$ in MeOH [5,6]) again provides indirect support for hydrogen transfer from the η^2-H_2.

$$'Ru(II)Cl'_2 + H_2 + base \longrightarrow 'Ru(H)Cl' + base \cdot HCl \qquad (10)$$

It should be noted that the kinetic data alone are equally well accommodated by a reaction sequence in which the roles of H_2 and styrene in Eqs. (3) and (4) are interchanged, i.e. an unsaturate route in which an initially formed Ru_2(styrene) species reacts with H_2. The estimated k_1, k'_{-1} and K values would then refer to formation of the Ru_2(styrene) adduct, but the spectroscopic data are incompatible with the formation of any such species.

The extent of applicability (if any) of the mechanism of Eqs. (3) and (4) within the more important asymmetric hydrogenations utilizing '$RuCl_2$(P–P)' systems, where P–P is a chiral phosphine such as chiraphos, diop, and binap [1–3], remains to be established. The $Ru_2Cl_4(P\text{–}P)_2$ complexes for all these chiral phosphines have been isolated [2], but reversible formation of an η^2-H_2 species (Eq. (1)) has been noted and studied only for the dppb system [this paper and refs. 7,13] and a related 1,4-bis(dicyclohexylphosphino) butane [13] system, both of which, like diop and binap systems, contain seven-membered chelate rings. The species corresponding to **2** but containing biphemp (2,2′-dimethyl-6,6′-bis(diphenylphosphino)biphenyl), analogous to binap and again giving a seven-membered chelate ring, has also been reported [27]. In addition to these seven-membered ring systems, the $Ph_2P(CH_2)_3PPh_2$ analogue of **1** (containing six-membered rings) reacts with H_2 according to Eq. (1) [13], while the chiraphos analogue (containing five-membered rings) reacts with H_2 in the presence of NEt_3 to give $[Ru(H)Cl(chiraphos)]_3$ [26] and, like the dppb system (see above), this, probably proceeds via the dinuclear η^2-H_2 intermediate.

4. Concluding remarks

Ruthenium(II) complexes containing one chelating ditertiary phosphine, or two monodentate tertiary phosphines, per metal are rich in molecular hydrogen chemistry, particularly dinuclear species containing ancillary chloro ligands [7,12,15,17,20,25,27], and the kinetic and mechanistic studies reported in this paper suggest very strongly that η^2-H_2 species are involved in the hydrogen-transfer process during catalytic hydrogenation. Our data are not as definitive as those reported for the $Ru(binap)(O_2CMe)_2$-catalyzed hydrogenation of unsaturated carboxylic acids, in which η^2-H_2 species are certainly not the direct hydrogen-transfer reagents. As in most well-studied catalytic hydrogenation systems, both "hydride" and "unsaturate" routes have been demonstrated for closely related systems (and sometimes within a single system, e.g. with $RhCl(PPh_3)_3$) [21], and the "Ru(P–P)" systems will undoubtedly show similar "bifunctional" mechanistic behavior, at least.

An open-minded approach to such studies is to be encouraged, as in all research. For an appropriate example, who would have considered that carbon monoxide could bind to a metal centre without significant π-bonding contributions, as observed by Fausto Calderazzo [28], whom we congratulate on his 65th birthday.

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