

Direct comparison between the mechanism of hydrometalation and β -elimination in heterogeneous and homogeneous hydrogenation

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Abstract

A novel approach has been developed to study hydrometalation by determining the location of deuterium on the double bond formed from the collapse of the metal–alkyl complex. This has allowed a direct comparison to be carried out between the mode of hydrometalation and geometry of β -elimination in homogeneous and heterogeneous hydrogenation. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hydrometalation; β -elimination; Hydrogenation; Homogeneous catalysis; Heterogeneous catalysis

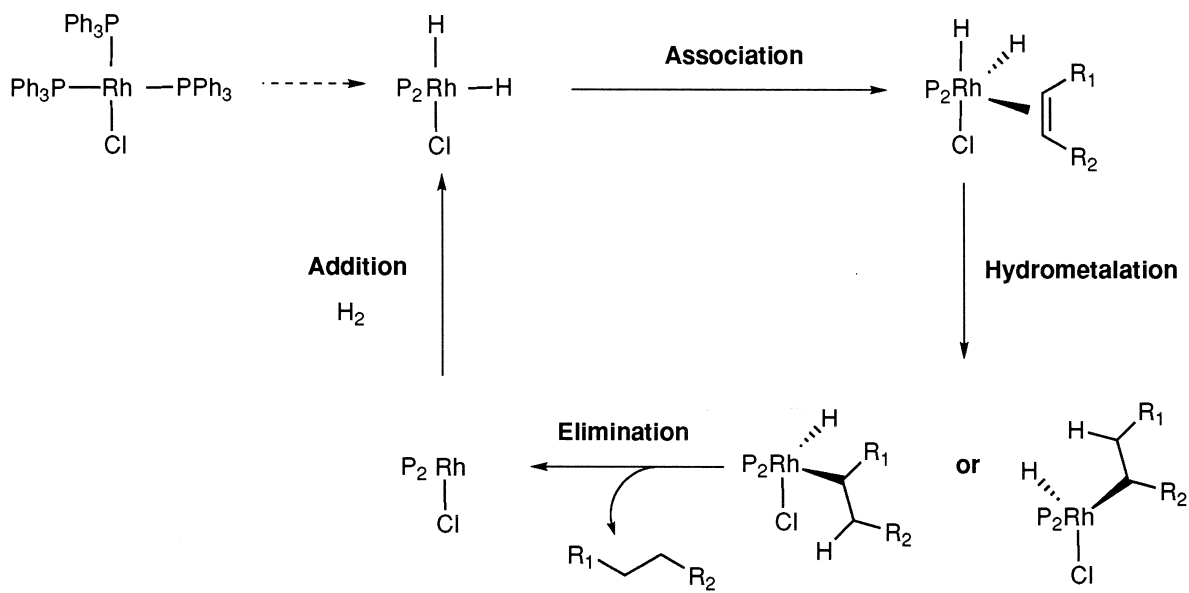
1. Introduction

The desire for superior hydrogenation catalysts has prompted an intense effort over the last two decades to gain a clear understanding of the mechanism of this reaction [1,2]. The mechanism put forward by Horiuti–Polanyi in 1934 for heterogeneous hydrogenation of ethene has been used widely as a framework to direct further studies [3]. This has led many surface scientists to focus on ethene in an attempt to elucidate the detailed steps of catalytic hydrogenation. One of the highlights of these studies has been the identification of a series of species

formed on the metal surface under UHV conditions, such as ethylidyne [4,5]. Although, the existence of these species have been clearly demonstrated under UHV conditions there is considerable doubt whether they are formed or involved in the pathway under normal hydrogenation conditions [6]. The reaction using homogeneous catalysts has also been vigorously studied and a general mechanism for this has been proposed (Scheme 1) [7]. The hydrometalation step gives two possible products owing to the metal hydrogen bond being able to add to the alkene both ways round. It is highly desirable to understand how steric and electronic effects control the orientation of hydrometalation.

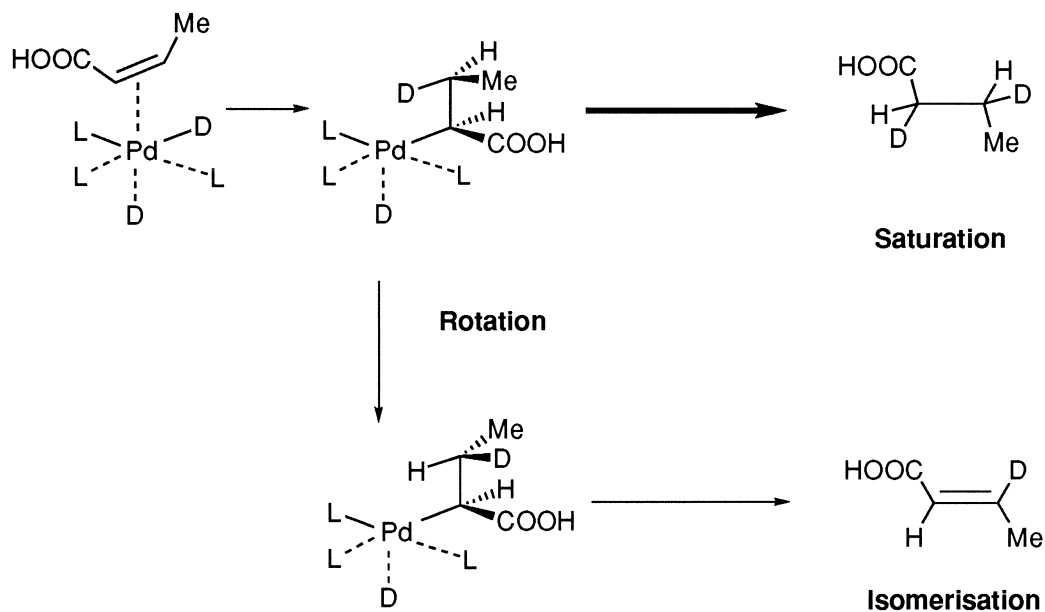
It has proved difficult to establish whether hydrometalation and β -elimination on the surface of metals is analogous to that occurring

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with homogeneous catalysts because the methods used to investigate one system have not been applicable to the other [8]. It is well documented in homogeneous systems that the

metal-alkyl complex intermediate formed by hydrometalation can either undergo reductive elimination to give the alkane or collapse back via β -elimination to give the alkene [9,10]. If a



cis-alkene is used the metal–alkyl complex intermediate formed can rotate to give the *trans* conformation which can either form the saturated product or form the double bond with the *trans* configuration by β -elimination (Scheme 2). By using deuterium gas and a *cis*-alkene the location of the deuterium on the double bond of the *trans*-alkene can determine the regioselectivity of hydrometalation [11,12]. This method can be applied to both heterogeneous and homogeneous systems under normal hydrogenation conditions making it possible to conduct a direct comparison between them.

2. Experimental

2.1. Materials

The *cis*-isomers of **1** and **3** were prepared by reduction of corresponding acetylenes over Lindlar catalyst and purified by preparative TLC [13]. The *cis*-isomer of **4** was obtained by photoisomerisation of the *trans* isomer purchased from Aldrich and purified by recrystallization and preparative TLC [14]. The *cis*-isomer of **5** was purchased from Aldrich and further purified by preparative TLC. Compounds **2**, **6**, **7** and the monosubstituted styrenes **8** were purchased from Aldrich and used without further purification. Palladium on charcoal (5%), palladium on charcoal (10%), Lindlar catalyst (5%), bis[1,2-bis(diphenylphosphino)-ethane]palladium(0) and deuterium gas were purchased from Aldrich. C₂H₅OD and benzene were purchased from Aldrich and dried over 4 Å molecular sieves. Anhydrous methanol stored over 4 Å molecular sieves was purchased from Fluka.

2.2. Measurement of deuterium incorporation

Deuterium incorporation was measured by integration of the respective ¹H NMR signals: (1) when only one position of the double bond was exchanged by deuterium (substrates **1**, **2**), the amount of deuterium incorporated was cal-

culated by referring to a full proton on the other position of the double bond. (2) When both positions of the double bond were exchanged by deuterium, the calculation was made by referring to another group within the molecule as an internal standard (**3**, **4**, **5**). Errors for the data are $\pm 5\%$.

2.3. Kinetic studies

Hydrogenations were performed using a standard atmospheric pressure hydrogenator to measure the volume of hydrogen consumed as a function of time, the height of the manometer reservoir being continually adjusted to maintain a hydrogen pressure of 1 atm. A constant reaction temperature was maintained by immersing the reaction vessel in a Grant W14 water bath. The reaction mixture was stirred at a uniform frequency using a Camlab Variomag[®] Telemodul 20P immersible magnetic stirrer.

3. Homogeneous hydrogenation

3.1. *trans*-Crotonic acid (**1**)

To a solution of *cis*-isomer of **1** (86 mg, 1 mmol) in benzene (3 ml) was added bis[1,2-bis(diphenylphosphino)-ethane]palladium(0) (68 mg). The mixture was degassed and refilled with D₂ via a balloon. The reaction mixture was stirred for 80 min at room temperature under 1 atm of D₂. The reaction mixture was then washed through a silica gel column with diethyl ether and solvent evaporated in vacuo at 0°C to give the product residue (79 mg) which was determined by ¹H NMR to consist of a mixture of 46% reduced product, 12% *cis*-isomer and 42% **1**. The pure form of **1** was obtained by preparative TLC, eluting with ethyl acetate–petroleum ether–methanol (9:15:0.1), which was then evaporated to dryness at 0°C and analyzed by ¹H NMR (data for both labelled and unlabelled **1** is given) and MS. $R_f = 0.23$; ¹H NMR (250 MHz, CDCl₃) δ 7.08 (dq, $J = 15.7, 7.2$

Hz, 1H), 5.83 (dq, $J = 15.7, 1.5$ Hz, 1H), 5.82 (q, $J = 1.5$ Hz, 1H), 1.90 (br, 3H, CH₃); HRMS (CI) m/z (M⁺) calcd. for C₄H₅²HO₂, 87.0431; found, 87.0430.

3.2. 4-Methoxystyrene (2)

To a solution **2** (134 mg, 1 mmol) in benzene (3 ml) was added bis[1,2-bis(diphenylphosphino)-ethane]palladium(0) (68 mg). The mixture was degassed and refilled with D₂ via a balloon. The reaction mixture was stirred for 15 min at room temperature under 1 atm of D₂. The reaction mixture was then washed through a silica gel column with diethyl ether and solvent evaporated in vacuo at 0°C to give the product residue (118 mg) which was determined by ¹H NMR to consist of a mixture of 85% reduced product and 15% **2**. ¹H NMR (250 MHz, CDCl₃) δ 7.35, 6.85 (ArH, 5H), 6.65 (m, 1H), 5.62 (d, $J = 17.6$ Hz, 1H), 5.61 (d, $J = 17.6$ Hz, 1H), 5.13 (d, $J = 11.1$ Hz, 1H), 5.12 (d, $J = 11.1$ Hz, 1H), 3.76 (s, OCH₃, 3H). HRMS (CI) m/z (M⁺) calcd. for C₉H₉²HO, 135.0795; found, 135.0765.

3.3. *trans*-Cinnamic acid (3)

To a solution of *cis*-isomer of **3** (148 mg, 1 mmol) in benzene (3 ml) was added bis[1,2-bis(diphenylphosphino)-ethane]palladium(0) (68 mg). The mixture was degassed and refilled with D₂ via a balloon. The reaction mixture was stirred for 30 min at room temperature under 1 atm of D₂. The reaction mixture was then washed through a silica gel column with diethyl ether and solvent evaporated in vacuo at 0°C to give the product residue (145 mg) which was determined by ¹H NMR to consist of a mixture of 91% reduced product and 9% **3**. The pure form of **3** was obtained by preparative TLC, eluting with ethyl acetate–hexane–methanol (100:30:0.5), which was then evaporated to dryness and analyzed by ¹H NMR (data for both labelled and unlabelled **3** is given) and MS. $R_f = 0.28$; ¹H NMR (250 MHz, CDCl₃) δ 7.79

(d, $J = 16.1$ Hz, 1H), 7.78 (br, 1H), 7.65–7.15 (ArH, 5H), 6.45 (d, $J = 16.1$ Hz, 1H), 6.44 (br, 1H). HRMS (CI) m/z (M⁺–H) calcd. for C₉H₆²HO₂, 148.0509; found, 148.0518.

3.4. *trans*-4-Methoxycinnamic acid (4)

To a solution of *cis*-isomer of **4** (178 mg, 1 mmol) in benzene (3 ml) was added bis[1,2-bis(diphenylphosphino)-ethane]palladium(0) (68 mg). The mixture was degassed and refilled with D₂ via a balloon. The reaction mixture was stirred for 45 min at room temperature under 1 atm of D₂. The reaction mixture was then washed through a silica gel column with diethyl ether and solvent evaporated in vacuo at 0°C to give the product residue (179 mg) which was determined by ¹H NMR to consist of a mixture of 75% reduced product and 25% **4**. The pure form of **4** was obtained by preparative TLC (reverse phase), eluting with ethyl acetate–hexane–methanol (10:100:4), which was then evaporated to dryness and analyzed by ¹H NMR (data for both labelled and unlabelled **4** is given) and MS. $R_f = 0.38$; ¹H NMR (250 MHz, CDCl₃) δ 7.89 (d, $J = 15.6$ Hz, 1H), 7.88 (br, 1H), 7.65, 7.27 (ArH, 4H), 6.37 (d, $J = 15.6$ Hz, 1H), 6.36 (br, 1H), 3.92 (s, OCH₃, 3H). HRMS (CI) m/z (M⁺–H) calcd. for C₁₀H₈²HO₃, 178.0615; found, 178.0622.

3.5. *trans*-β-Methoxystyrene (5)

To a solution of *cis*-isomer of **5** (134 mg, 1 mmol) in benzene (3 ml) was added bis[1,2-bis(diphenylphosphino)-ethane]palladium(0) (68 mg). The mixture was degassed and refilled with D₂ via a balloon. The reaction mixture was stirred for 40 min at room temperature under 1 atm of D₂. The reaction mixture was then washed through a silica gel column with diethyl ether and solvent evaporated in vacuo at 0°C to give the product residue (179 mg) which was determined by ¹H NMR to consist of a mixture of 26% reduced product, 62% *cis*-isomer and 12% **5**. The pure form of **5** was obtained by

preparative TLC, eluting with hexane, which was then evaporated to dryness and analyzed by ^1H NMR (data for both labelled and unlabelled **5** is given) and MS. $R_f = 0.10$; ^1H NMR (250 MHz, CDCl_3) δ 7.60, 7.30, 7.15 (ArH, 5H), 7.06 (d, $J = 13.0$ Hz, 1H), 7.06 (t, $J = 3.5$ Hz, 1H), 5.83 (d, $J = 13.0$ Hz, 1H), 5.81 (t, $J = 3.5$ Hz, 1H), 3.72 (s, OCH_3 , 3H). HRMS (CI) m/z (M^+) calcd. for $\text{C}_9\text{H}_9^2\text{HO}$, 135.0795; found, 135.0800.

4. Heterogeneous hydrogenation

4.1. *trans*-Cinnamic acid (**3**)

To a solution of *cis*-isomer of **3** (148 mg, 1 mmol) in $\text{C}_2\text{H}_5\text{OD}$ (3 ml) was added 10% Pd/C (3 mg). The mixture was degassed and refilled with D_2 via a balloon. The reaction mixture was stirred for 50 min at room temperature under 1 atm of D_2 . The reaction mixture was then filtered to remove the catalyst and solvent evaporated in vacuo at 0°C to give the product residue (142 mg) which was determined by ^1H NMR to consist of a mixture of 15% *cis*-isomer, 80% reduced product and 5% **3**. The pure form of **3** was obtained by preparative TLC, eluting with ethyl acetate–hexane–methanol (100:30:0.5), which was then evaporated to dryness and analyzed by ^1H NMR (data for both labelled and unlabelled **3** is given) and MS. $R_f = 0.28$; ^1H NMR (250 MHz, CDCl_3) δ 7.79 (d, $J = 16.1$ Hz, 1H), 7.78 (br, 1H), 7.65–7.15 (ArH, 5H), 6.45 (d, $J = 16.1$ Hz, 1H), 6.44 (br, 1H). HRMS (CI) m/z ($\text{M}^+ - \text{H}$) calcd. for $\text{C}_9\text{H}_6^2\text{HO}_2$, 148.0509; found, 148.0520.

4.2. *trans*-4-Methoxycinnamic acid (**4**)

To a solution of *cis*-isomer of **4** (178 mg, 1 mmol) in $\text{C}_2\text{H}_5\text{OD}$ (3 ml) was added 10% Pd/C (3 mg). The mixture was degassed and refilled with D_2 via a balloon. The reaction mixture was stirred for 25 min at room temperature under 1 atm of D_2 . The reaction mixture

was then filtered to remove the catalyst and solvent evaporated in vacuo at 0°C to give the product residue (176 mg) which was determined by ^1H NMR to consist of a mixture of 20% *cis*-isomer, 73% reduced product and 7% **4**. The pure form of **4** was obtained by preparative TLC (reverse phase), eluting with ethyl acetate–hexane–methanol (10:100:4), which was then evaporated to dryness and analyzed by ^1H NMR (data for both labelled and unlabelled **4** is given) and MS. $R_f = 0.38$; ^1H NMR (250 MHz, CDCl_3) δ 7.89 (d, $J = 15.6$ Hz, 1H), 7.88 (br, 1H), 7.65, 7.27 (ArH, 4H), 6.37 (d, $J = 15.6$ Hz, 1H), 6.36 (br, 1H), 3.92 (s, OCH_3 , 3H). HRMS (CI) m/z ($\text{M}^+ - \text{H}$) calcd. for $\text{C}_{10}\text{H}_8^2\text{HO}_3$, 178.0615; found, 178.0610.

4.3. *trans*- β -Methoxystyrene (**5**)

To a solution of *cis*-isomer of **5** (134 mg, 1 mmol) in benzene (3 ml) was added 10% Pd/C (3 mg). The mixture was degassed and refilled with D_2 via a balloon. The reaction mixture was stirred for 45 min at room temperature under 1 atm of D_2 . The reaction mixture was then filtered to remove the catalyst and solvent evaporated in vacuo at 0°C to give the product residue (129 mg) which was determined by ^1H NMR to consist of a mixture of 12% *cis*-isomer, 80% reduced product and 8% **5**. The pure form of **5** was obtained by preparative TLC, eluting with hexane, which was then evaporated to dryness and analyzed by ^1H NMR (data for both labelled and unlabelled **5** is given) and MS. $R_f = 0.10$; ^1H NMR (250 MHz, CDCl_3) δ 7.60, 7.30, 7.15 (ArH, 5H), 7.06 (d, $J = 13.0$ Hz, 1H), 7.06 (t, $J = 3.5$ Hz, 1H), 5.83 (d, $J = 13.0$ Hz, 1H), 5.81 (t, $J = 3.5$ Hz, 1H), 3.72 (s, OCH_3 , 3H). HRMS (CI) m/z (M^+) calcd. for $\text{C}_9\text{H}_9^2\text{HO}$, 135.0795; found, 135.0806.

4.4. 2-Cyclohexen-1-one (**6**)

To a solution of **6** (96 mg, 1 mmol) in $\text{C}_2\text{H}_5\text{OD}$ (3 ml) was added 10% Pd/C (3 mg).

The mixture was degassed and refilled with D₂ via a balloon. The reaction mixture was stirred for 30 min at room temperature under 1 atm of D₂. The reaction mixture was then filtered to remove the catalyst and solvent evaporated in vacuo at 0°C to give the product residue (89 mg) which was determined by ¹H NMR to consist of a mixture of 20% **6** and 80% reduced product. ¹H NMR shows that there is no detectable deuterium incorporation on the double bond of **6**.

4.5. 3,4-Dihydro-2H-pyran (**7**)

To a solution of **7** (84 mg, 1 mmol) in benzene (3 ml) was added 10% Pd/C (3 mg). The mixture was degassed and refilled with D₂ via a balloon. The reaction mixture was stirred for 30 min at room temperature under 1 atm of D₂. The reaction mixture was then filtered to remove the catalyst and solvent evaporated in vacuo at 0°C to give the product residue (70 mg) which was determined by ¹H NMR to consist of a mixture of 55% **7** and 45% reduced product. ¹H NMR shows that there is no detectable deuterium incorporation on the double bond of **7**.

5. Typical procedures for the addition of electron donating ligands into heterogeneous system

5.1. *trans*-β-Methoxystyrene (**5**)

To a solution of *cis*-isomer of **5** (134 mg, 1 mmol) in benzene (3 ml) was added 10% Pd/C (20 mg) and quinoline (39 mg, 0.3 mmol). The mixture was degassed and refilled with D₂ via a balloon. The reaction mixture was stirred for 2 h at room temperature under 1 atm of D₂ followed by removal of the catalyst by filtration. Solvent was evaporated from the filtrate to give a mixture of quinoline and the product (162 mg) which was determined by

¹H NMR to consist of 40% reduced product, 48% *cis*-isomer and 12% *trans*-isomer. The pure form of the *trans*-isomer was obtained by silica column chromatography eluting with hexane and the incorporation of the deuterium at each position on the double bond was determined by ¹H NMR as described, using the methyl group as an internal standard. For the experiment performed using 100 mM quinoline, samples were taken at intervals over the whole course of the reaction. The deuterium distribution across the double bond was found not to vary with reaction time.

5.2. *trans*-β-Methoxystyrene (**5**)

To a solution of *cis*-isomer of **5** (134 mg, 1 mmol) in benzene (3 ml) was added 10% Pd/C (20 mg) and triphenylphosphine (20 mg, 0.08 mmol). The mixture was degassed and refilled with D₂ via a balloon. The reaction mixture was stirred for 2 h at room temperature under 1 atm of D₂ followed by removal of the catalyst by filtration. Solvent was evaporated from the filtrate to give a mixture of triphenylphosphine and the product (146 mg) which was determined by ¹H NMR to consist of 40% reduced product, 50% *cis*-isomer and 10% *trans*-isomer. The pure form of the *trans*-isomer was obtained by silica column chromatography eluting with hexane and the incorporation of the deuterium at each position on the double bond was determined by integration of the respective ¹H NMR signals, using the methyl group as an internal standard.

6. Typical procedure for the measurement of the rate of reduction of various monosubstituted styrenes

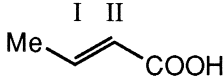
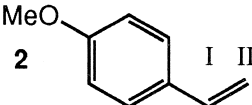
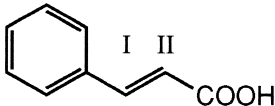
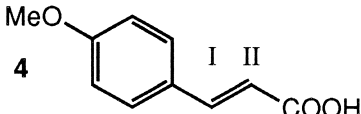
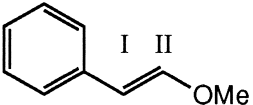
6.1. Hydrogenation of styrene

Five percent Palladium on charcoal (5.000 mg) was suspended in anhydrous methanol (2 ml) and the mixture stirred at 300 rpm at 25°C.

The system was degassed and then argon introduced at 1 atm. This cycle was repeated three times. The system was then degassed followed by introduction of hydrogen at 1 atm, this cycle also being repeated three times. The reaction mixture was allowed to stir under this atmosphere for 5 min to allow adsorption of hydrogen on the catalyst surface to equilibrate. The aqueous copper(II) sulfate manometer was then filled with hydrogen and the height of the

manometer reservoir adjusted to give a starting hydrogen pressure of 1 atm. A solution of styrene (208 mg, 2 mmol) in anhydrous methanol (2 ml) was then added by syringe and timing immediately started. The volume of hydrogen consumed was noted at 1 min intervals until approximately 50% conversion of starting material (ca. 12 min). The procedure was repeated four times and a mean rate constant (unit = ml/min) calculated.

Table 1
Deuterium incorporation into *trans*-alkenes using homogeneous catalysts

	PRODUCT	DEUTERIUM DISTRIBUTION (%)		RELATIVE RATIO OF DEUTERIUM (%)	
		I	II	I	II
1		64	0	100	0
2		0	<i>Cis</i> 32* <i>Trans</i> 32	0	100
3		37	6	86	14
4		22	24	48	52
5		37	4	90	10

* *cis/trans* refers to the deuterium being *cis/trans* to the aromatic group. Some compounds were identified with 2 deuteriums in the terminal position of the double bond. The proportion of this compound increased with a longer reaction time as did that of the mono-deuterated species.

7. Results and discussion

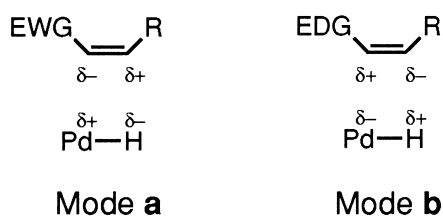
7.1. Hydrometalation

When our approach was used to investigate the mechanism of hydrometalation using a homogeneous catalyst it was found that the regioselectivity of hydrometalation is greatly influenced by the polarisation of the double bond [11,12]. If an electron withdrawing group, such as a carboxyl group in compound **1** (Table 1), is attached to the double bond hydrometalation takes place with the addition of deuterium remote to the electron withdrawing group and the metal next to it. This suggests that the dipole of the double bond induces the metal hydrogen bond to be polarised so that the metal is electropositive and the hydrogen electronegative (**mode a** $\text{Pd}^{\delta+}-\text{H}^{\delta-}$, Scheme 3). Remarkably, the metal hydrogen bond can be polarised the opposite way round (**mode b** $\text{Pd}^{\delta-}-\text{H}^{\delta+}$, Scheme 3) when an electron donating group such as an aromatic group in compound **2** is attached to the double bond (Table 1). When alkenes with two functional groups conjugated to the double bond were used, it was found that both modes of hydrometalation can take place (Table 1). With cinnamic acid **3** deuterium is found mainly remote to the carboxyl group which reports that this catalyst operates predominantly by **mode a** with this substrate. Compound **4** differs from cinnamic acid only by having a para methoxy group on the aromatic

ring but results in a large increase in hydrometalation occurring by **mode b**. This can only be explained by the increase in the electron donating ability of the aromatic ring enhancing addition by this mode. Steric effects cannot play a major role in the change in regioselectivity of hydrometalation between compounds **3** and **4** because the methoxy group is too distant from the double bond to interfere. The enol ether **5** is strongly polarised so that the carbon next to the methoxy group is electron deficient and that next to the phenyl group electron rich. It is found with the palladium catalyst that hydrometalation of the enol ether occurs nearly exclusively by **mode b**. The combined results show that the palladium hydrogen bond is amphipolar with this homogeneous catalyst and suggests that hydrometalation occurs by a two electron process.

Use of the same difunctional alkenes with different catalysts provides a sensitive assay to probe the **mode** preference of a particular catalyst and hence insight into the intrinsic electronic property of the catalyst. To directly compare the homogeneous palladium catalyst with heterogeneous palladium on carbon the isomerisation of the *cis* isomers of alkenes **3–5** was performed with the heterogeneous catalyst and deuterium gas. The results show that the regioselectivity of hydrometalation is similar to that found with the homogeneous catalyst and suggest that the palladium hydrogen bond is also amphipolar with the heterogeneous catalyst (Table 2). The comparison however reveals that with heterogeneous palladium, there is a definite shift towards **mode b** relative to the homogeneous catalyst.

The observed differences in hydrometalation between the two catalysts could be a result of the phosphine ligands donating electrons into the palladium atom of the homogeneous catalyst and promoting **mode a** by stabilisation of the electron deficient metal centre. To test this theory various compounds that could act as ligands to the palladium in the heterogeneous catalyst were used as additives and the regioselectivity

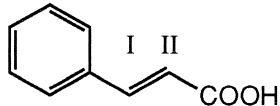
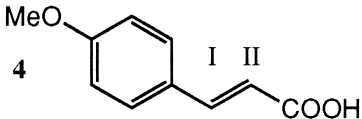
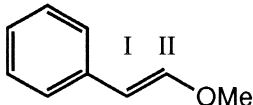


EWG = electron withdrawing group

EDG = electron donating group

Scheme 3.

Table 2
Deuterium incorporation into *trans*-alkenes using Pd/C

PRODUCT	DEUTERIUM DISTRIBUTION (%)		RELATIVE RATIO OF DEUTERIUM (%)	
	I	II	I	II
	29	30	49	51
	8	47	15	85
	56	1	98	2

of hydrometalation determined. It is found that the addition of quinoline leads to a dramatic shift towards **mode a** (Table 3). A similar result was also found with triphenylphosphine which confirms that these strong ligands alter the intrinsic electronic properties of the palladium catalyst.

It is well known that quinoline and triphenylphosphine are used as additives to improve the selectivity of catalysts for the semi-reduction of alkynes to *cis*-alkenes [1]. Previous researchers have tried to rationalise this suggesting that quinoline either modifies the surface structure of the catalyst or selectively blocks the

Table 3
Effect of quinoline and triphenylphosphine of the mode of hydrometalation

Ligand	Concentration (mM)	Deuterium distribution (%)		Relative ratio of deuterium (%)	
		I	II	I	II
Quinoline	0	56	1	98	2
	50	50	19	72	28
	100	36	27	57	43
	150	36	27	57	43
Triphenylphosphine	25	30	22	58	42

adsorption of the *cis*-alkenes [15–17]. Alkynes are reported to be more reactive towards nucleophiles than alkenes [18]. We therefore propose that quinoline has effectively increased the nucleophilicity of the palladium hydrogen species by promoting **mode a**, leading to better selectivity for the reduction of alkynes [19].

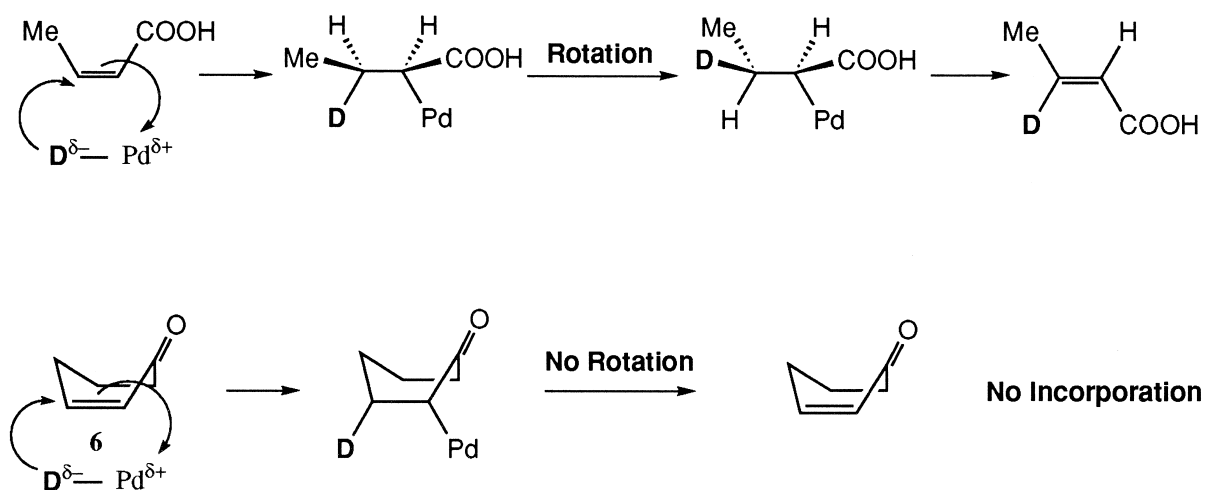
The identification of the amphipolar nature of the palladium hydrogen bond and how it may be influenced by ligands should allow for the rational design of catalysts with defined electronic properties.

7.2. β -Elimination

In homogeneous catalysis, it has been rigorously shown that β -elimination takes place with *syn* geometry [9,10]. Since β -elimination is the reverse of hydrometalation the elucidation of this process with heterogeneous catalysts is critical for a clear understanding of the mechanism of catalytic hydrogenation. Some evidence for β -elimination occurring on the surface of metals was obtained by studying the decomposition of chemisorbed alkyls generated from ethyl iodide and platinum under UHV conditions [20]. Further investigation on the rate difference of β -elimination between chemisorbed alkyl and cy-

cloalkyl groups on Cu(100) suggests that planarity of the transition state of this step is required [21,22]. β -Elimination is rigorously discussed and presumed to occur with *syn* geometry in a study on the stereochemistry of addition of H atoms to alkenes on a Cu(100) surface (top face or bottom face) where the H atoms are generated from dissociation of H₂ by a hot tungsten filament [23].

The approach used in this study reveals the precise orientation of hydrometalation and therefore facilitates investigation into details of how the palladium–alkyl complex formed by hydrometalation collapses back to give the alkene. All the *cis*-alkenes **1–5** hydrogenated using deuterium result in label being incorporated into the *trans*-alkene. When *cis*-alkene is isolated by stopping the reaction before completion, there is no detectable incorporation of deuterium on the *cis*-double bond. This suggests that the intermediate palladium–alkyl complex can only undergo *syn* elimination which requires removal of the hydrogen *cis* to the palladium. To further test this hypothesis, two cyclic alkenes, **6** and **7**, were hydrogenated using deuterium. Note that the functional group adjacent to the double bond fixes the regiochemistry of hydrometalation [12] and the cyclic system fixes



Scheme 4.

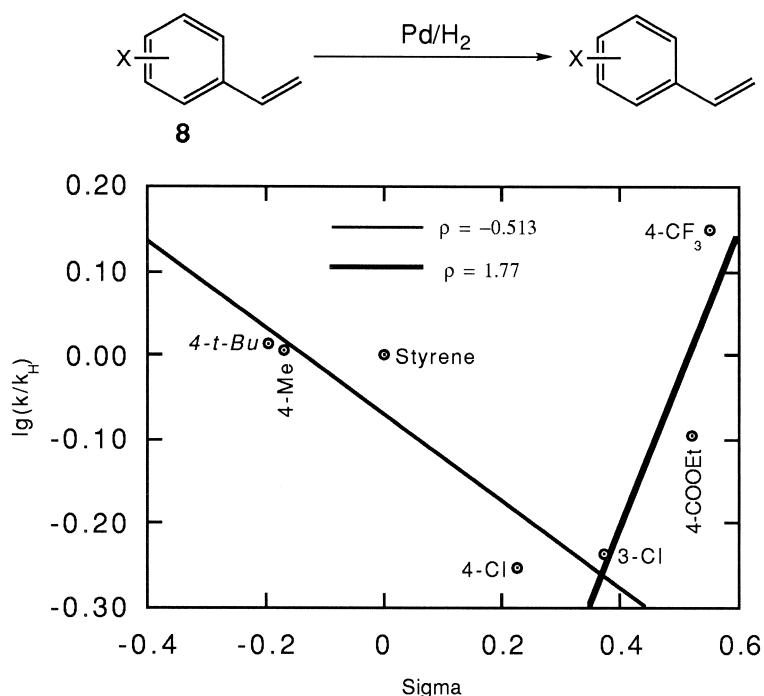


Fig. 1. Hammett plot for hydrogenation of monosubstituted styrenes **8** using 5% Pd on charcoal as catalyst [25].

the geometry of the palladium–alkyl intermediate by preventing rotation from occurring. If elimination takes place with syn geometry, no deuterium incorporation will be observed, whereas anti-elimination should give incorporation (Scheme 4). The results show that with palladium on carbon there is no deuterium incorporation into either of the cyclic alkenes, **6** and **7**, thus suggesting that β -elimination occurs with syn geometry in both homogeneous and heterogeneous systems.

7.3. Electronic effects on the rate of reduction of various substituted styrenes: Hammett plot

It has been observed using homogeneous catalysts that the rate of reduction of differently substituted styrene molecules increases with both electron donating and electron withdrawing groups on the aromatic ring [24]. This could be explained by the opposing trends in rate constants for binding to the metal and hydrometala-

tion. However, it is possible in the light of the observation that there are two modes of hydrometalation (**mode a** Pd ^{$\delta+$} –H ^{$\delta-$} and **mode b** Pd ^{$\delta-$} –H ^{$\delta+$}) that rate enhancement by either electron withdrawing or donating groups could be due to operation of **mode a** and **mode b**, respectively.

To complement this work, we have investigated the dependence of rate of reduction of substituted styrenes using a heterogeneous hydrogenation catalyst (Pd/C). The Hammett plot obtained gives a V shape graph, which again is consistent with a switch from one mode of hydrometalation to the other when the polarity of the double bond is altered (Fig. 1).

8. Conclusion

A new approach has been developed to investigate the mechanism of hydrometalation and β -elimination in both homogeneous and hetero-

geneous hydrogenation of alkenes. The regioselectivity of hydrometalation is determined by the location of the deuterium atom on the *trans* double bond formed by the collapse of the metal–alkyl complex. The Pd–H bond in both homogeneous and heterogeneous catalysis is found to be amphipolar with hydrometalation taking place either by **mode a** or **mode b** depending on the polarity of the alkene double bond. Comparison between the two systems show that homogeneous catalysts favour **mode a** which can be rationalised by donation of electrons from the phosphine ligands helping to stabilise the electron deficient centre in **mode a**. A similar electronic effect is found if hydrogenation additives quinoline and triphenylphosphine are present with heterogeneous catalysts. This provides a possible rationale for how these additives improve the selectivity of the semi-hydrogenation of alkynes to *cis*-alkenes. The lack of deuterium incorporation using cyclic alkenes strongly suggests that β -elimination occurs with syn elimination in heterogeneous systems as it does in homogeneous systems.

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