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Ruthenium diphosphine complexes for catalysis; a general synthesis and direct comparisons with rhodium complexes

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Abstract. A method for the preparation of diphosphineruthenium complexes from a range of diphosphine precursors is described. The stable products, of general formula $P_2Ru(allyl)acac$ (P = phosphine ligand), do not catalyse the hydrogenation of alkenes but can easily be converted into catalytically active species by reaction with trimethylsilyl trifluoromethanesulfonate. The chemistry involved in this transformation is discussed. Catalysis of the hydrogenation of a range of alkenes, and direct comparison with related rhodium reductions, is described. Some mechanistic insights are gained through additions of D_2 to alkenes and parallel hydrogenations on deuterated solvent, supporting the intervention of conventional dihydride and alkyl hydride intermediates which undergo exchange with solvent at both stages.

Introduction

Since their introduction a few years ago, ruthenium complexes of the ligand BINAP [a] and its close relatives have consistently set the benchmark for asymmetric hydrogenation[1]. In comparison to their rhodium counterparts of longer standing, the ruthenium catalysts are capable of the reduction of a much wider range of functional alkenes, including some classes which bind only weakly to the metal. Furthermore, they are very effective catalysts for the hydrogenation of ketones which bear a potential metal-binding group, especially β-ketoesters. Their qualities have generated much interest in applications over the range of scale from laboratory to plant[2]. For rhodium-complex catalysed, asymmetric hydrogenation, the reaction mechanism is moderately well understood, and remaining discussion is likely to focus on details rather than principle[3]. This is certainly not the case in ruthenium chemistry, and rather few papers with serious mechanistic content have been published[4]. There are interesting differences between Rh and Ru catalysts which remain to be explained, as follows:

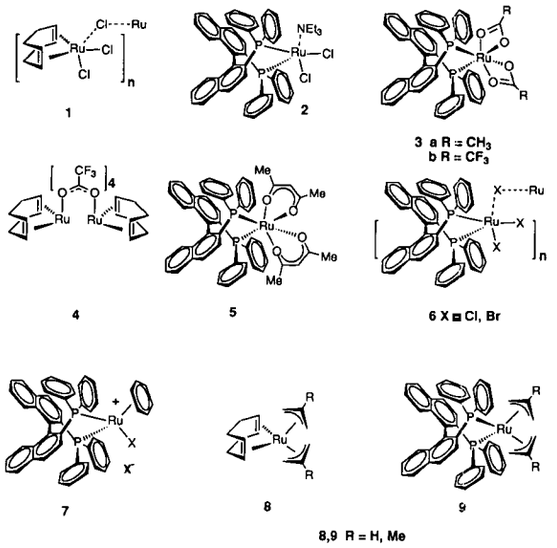
(a) For a given hand of ligand, the stereochemical outcome is opposite for the two metals.
(b) Whilst the enantiomer excess in Rh hydrogenations is very susceptible to fine tuning by ligand variation, in Ru hydrogenations only BINAP (or closely related atropisomeric diphosphines) are highly effective.
(c) In Ru hydrogenations, the configuration of the product for a series of related alkenes can depend on the substitution pattern about the double bond.

Mechanistic studies in rhodium chemistry have been greatly facilitated by the accessibility of a catalyst precursors $[P_2Rh(alkene)_2]$ (P = phosphine ligand) which render the true intermediates of the catalytic cycle amenable to direct observation. In ruthenium hydrogenations, the coordination chemistry leading to catalyst precursors is much less straightforward, and the main routes which have been developed are summarised here. The earliest Ru asymmetric hydrogenation chemistry utilised the polymeric cyclooctadiene complex of $RuCl_2$ as starting material, demonstrating that the reaction of complex **1** with BINAP in the presence of NEt_3 gave the orange-red complex **2**, effective in hydrogenation of enamides[5]. This complex was effectively superseded by diacetate **3a**, which was first prepared from the same precursor, save that a displacement reaction with NaOAc was carried out in the final step[6]. In some cases the related bis(trifluoroacetate) **3b** was a superior catalyst[7]. These complexes, and those of related atropisomeric ligands, could be prepared in a high state of purity by a systematic route which depends on the synthesis of the bridging trifluoroacetate **4**, which serves as a precursor to both **3a** and **3b**[8]. Three convenient routes to complex **3a** or analogues have been published, starting from $[(C_6H_6)RuCl_2]_2$, its DMSO complex, or by carrying out the original procedure for long periods in the absence of NEt_3 and the presence of toluene[9,10,11]. An alternative catalyst precursor **5** may be generated *in situ* at high pressures of H_2 from $Ru(acac)_3$ and BINAP in MeOH; the intermediate can be isolated in the absence of substrate[12]. For ketone reductions, the acetates and their analogues do not work particularly well and complex **6**, which is better prepared from **3a** rather than directly, is preferred[13]. For reasons of experimental convenience, they have been replaced by the cationic arene complexes typified by **7** which is in turn prepared from the readily synthesised $areneRuCl_2$ dimer[14].

With the exception of the acetylacetonates [b] and the

[a] BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthalene.

[b] Acetylacetonate = pentane-2,4-dionate.



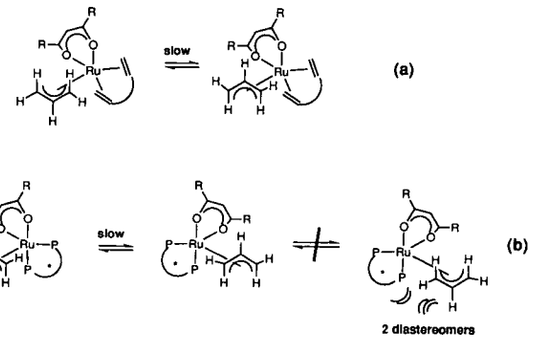


Figure 1. The origin of stereoisomerism in Ru allyl acetylacetonate complexes. For the diolefin complexes in ***a****, both diastereomers are energetically feasible. For the diphosphine complexes in* ***b****, a chiral ligand permits a total of four diastereomers because the Ru becomes an additional stereogenic centre. For steric reasons, only two of the four are accessible (cf, the X-ray structure of* **12a** *reported in Ref. 16).*

DMSO [c] complexes described above, none of these intermediates had proven generality for the synthesis of diphosphineruthenium complexes. A method which overcomes this problem was introduced by *Genet* and coworkers[15], who showed that thermolysis of a mixture of complex **8** (also used as an intermediate in the synthesis of the bridged species **4**) and a range of chelating ligands led to the isolation of complexes of type **9**. More vigorous conditions are required for the synthesis of the BINAP complex shown although other biphosphine Ru bis-allyls are formed on extended heating to 50°C in hexane. The allyl complexes can also be converted into the corresponding haloruthenium(II) catalysts by reaction with the corresponding protic acid.

Synthesis of ruthenium catalyst precursors

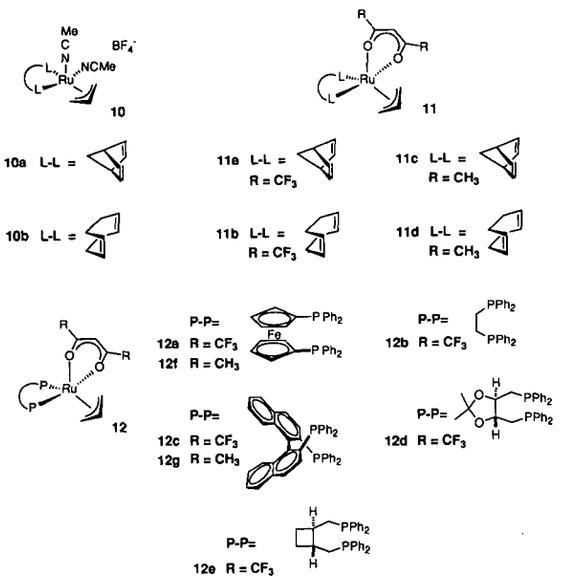
The long-term objective of our work in ruthenium chemistry[16] has been to develop a mechanistic understanding of this highly efficient, asymmetric hydrogenation in comparison to the established case of rhodium complexes. At the same time, we were concerned to develop more general methods for the synthesis of ruthenium catalysts so that new ligands could be evaluated; the ideal would combine the specificity of BINAP with higher reactivity, the latter perhaps associated with increased flexibility in the backbone. In order to facilitate these two objectives, a general synthesis of catalyst precursors was developed. In essence, this involves taking the chemistry developed by Lewis and co-workers twenty years ago[17] to provide the easily accessible cationic precursors **10a** or **10b**. These were then allowed to react with the sodium salt of acetylacetone or its hexafluoro analogue to provide stable complexes **11a-d**, of which **11d** had been previously reported. In the ^{1}H-NMR spectrum of **11b** in CD_2Cl_2, the existence of two diastereomers in the ratio 5/1 could clearly be discerned; for example, the characteristic multiplet due to the central CH of the allyl was at δ 4.98 in the minor species and at δ 4.70 in the major species; similar splittings could be seen for the remaining allyl protons, several of the cyclooctadiene protons, and interestingly for the central proton of the F_6acac moiety [δ 5.9 (major) 5.77 (minor)]. For the less sterically demanding norbornadiene complex **12a**, the diastereomer ratio in C_6D_6 was 1.7/1. It had been reported that the replacement of the diene ligand in complex **11d** by diphosphines did not occur cleanly, in contrast to the displacement by 2,2'-bipyridine. In our hands the first experiment attempted was between 1,1'-bis(diphenylphosphino)ferrocene and **11b**, refluxing for 5 hours in THF solution. A new product was isolated in 85% yield, which had the structure **12a**. The reaction could be conveniently followed by ^{31}P-NMR, and in achiral cases such as this a single product was observed as an AB quartet; when the diphosphine was chiral, two non-interconverting diastereomers were seen. The origins of this effect are clearly demonstrated by analysis of the X-ray crystal structure[16], showing that one of the P-Ru bonds is *trans* to an acetylacetonate O-Ru. The allyl must then sit with one terminal carbon *trans* to O, and the other *trans* to P, and allyl rotation in an achiral diphosphine complex like **12a** interconverts its enantiomers. For the complex of a chiral diphosphine, this process interconverts the two possible diastereomers. Implicit in this explanation is that two of the four possible rotamers in **12a** are inaccessible (Figure 1) In the precursor complexes **11**, the corresponding allyl rotamers are both populated, and interconversion is slow, leading to the observation of diastereomers in that series. The range of complexes synthesised by this method and their spectroscopic properties, is summarised in the experimental section.

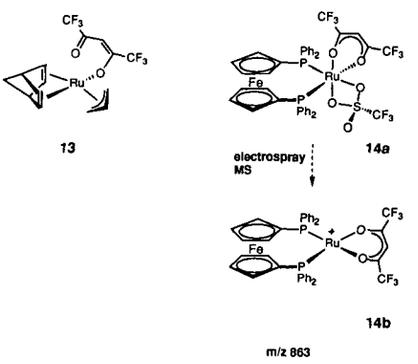
Comparison of the reactivity of different ligands and precursors in synthesis of the acac and F_6acac complexes **12** is of interest. Monitoring the reaction between the NBD [d] complex **11a** and FcP_2 by ^{31}P-NMR indicated a first-order dependence on the concentration of residual phosphine, supporting the idea of a dissociative process. At ambient temperature in THF, the half-time of reaction is about 25 min. The corresponding reaction of **11d** with FcP_2 is substantially slower, requiring several hours at reflux in THF to reach completion. Likewise, the COD [e] F_6acac complex **11b** reacted much more slowly with FcP_2, requiring several hours reflux in THF. With BINAP as ligand the reactions in THF were much slower, **11a** being completely consumed after 20 hours at reflux, but the reaction of **11c** was still only 70% complete after 94 hours reflux. On the basis of these limited observations the qualitative trends of F_6acac > acac and NBD $\gg$ COD are indicated. The trends could be explained if a critical step in the synthesis was the partial dissociation of the diketonate moiety to give a coordinatively unsaturated intermediate **13** which was attacked by the diphosphine. If the

[c] DMSO = dimethyl sulphoxide.

[d] NBD = bicyclohepta[2.2.1]diene.

[e] COD = cycloocta-1,5-diene.





diphosphine is sufficiently non-bulky, then the dissociative event is the rate-determining step.

Activation of complexes 12 for catalytic hydrogenation

Although the diphosphine complexes **12** can be used directly as catalysts for transfer hydrogenation[16] with $HNEt_3^+/HCO_2^-$, they are unreactive towards H_2 in the presence of alkenes at pressures close to ambient. Hence, electrophilic activation was attempted, the aim being to remove either the acac or allyl ligand to generate an active catalyst. By trial and error it was found that the best method for doing this (*vide infra*) was to react the complex with a twofold excess of trimethylsilyl trifluoromethanesulphonate (TMSOTf) in dichloromethane. Evacuation of reagent and solvent gave a species which was used immediately by dissolution with the reactant, normally in methanol, and then stirred under H_2. This raises the question of the nature of the activated species, which was addressed by NMR studies.

The ^{31}P-NMR spectrum of complex **12a** in CD_2Cl_2 was a non-dynamic double doublet at ambient temperature, δ 62.3, 28.0 ppm (J_{PP} 35 Hz), which became broad and featureless after reaction with excess TMSOTf. On cooling to -40°C, the sharpness was restored, but the high-field signal had shifted downfield by 12 ppm δ 58.2, 40.9 ppm (J_{PP} 39 Hz). Likewise, the ^{19}F spectrum before activation consists of two singlets at -79.1 and -80.4 ppm; after activation the main signal was at -82.0 ppm (OTf), with a second signal at -76.3 ppm (F_6acac). This implies a new species in which the allyl group has been replaced by OTf, and the acac remains intact (assuming that the high-field signal in the reactant **12a** is trans to C, and the low-field *trans* to O). Similar changes take place when complex **12a** is allowed to react with trityl [f] fluoroborate in CH_2Cl_2, the main differences being that the new species is only formed completely after 18 hours and that the spectrum is non-dynamic. Similarly, the reaction of complex **12f** with TMSOTf occurs to give an intermediate which has two distinct C-Me groups associated with the acac, and which thus remains coordinated.

Electrospray mass spectral analysis of the reactive intermediate proved informative. When complex **12a** was allowed to react with 2 or more equivalents of TMSOTf in CH_2Cl_2, and the solvent removed after several minutes followed by dissolution in MeOH, the mass spectrum showed a single cation corresponding to $[P_2Ru(F_6acac)]$ in mass- and isotope-distribution pattern. We interpret this to indicate that the allyl group is removed during the activation process and replaced by the triflate, possibly chelate coordinated as in **14a** but labile[18]. In dilute MeOH solution (the conditions of the electrospray MS probe), the OTf dissociates. giving the observed molecular ion to which we assign the structure **14b**.

Directed hydrogenation

Previous work had indicated that the course of homogeneous hydrogenation can be influenced by functional groups at an adjacent stereogenic centre, using Rh or Ir complex catalysts[19]. Similar effects, due to binding of the functional group to the metal centre during the catalytic cycle, had been reported for Ru-BINAP reductions[20]. Only the OH group was demonstrated to be effective there, whilst directing effects by a wide range of groups including CO_2R, $CONR_2$ NHCOR and SOR had been demonstrated in the rhodium and iridium reductions. Internal competition for the metal between different groups was of interest, and thus the reactions of Figure 2 were examined. If the hydroxyl group controls the stereochemical course of hydrogenation of compound **15**, then the product **16** has $2R^*,3S^*$ configuration, but if the methoxycarbonyl group is coordinated, then the $2R^*,3R^*$ diastereomer of **16** is formed. The relative configuration of the two stereogenic centres in the product can be determined by comparison with literature ^{1}H and ^{13}C data[21].

Hydrogenations were carried out in a constant-volume apparatus[22] with an initial pressure of about 1600 mbar., employing 3 mol% of the TMSOTf-activated catalyst **12a** in MeOH solution. Following the reaction against time at 30°C, there was a short induction period and then the requisite amount of H_2 was taken up over 100 minutes, in a process close to first order in reactant. This implied that the reactant **15** was not tightly bound to Ru during the catalytic cycle. NMR analysis indicated that the product was a 92/8 mixture favouring the $2R^*,3R^*$ isomer of **16**. This indicates that the stereochemical course of reaction is controlled by the carbonyl group. Since the Lewis basicity of the two residues OH and CO_2Me is similar, their relative coordinating power is probably less important than the relative stability of the chelate ring formed. The inset [α] to Figure 2 shows the intermediate which leads to the preferred product. Repeating the reaction under otherwise identical conditions but with catalyst **12f**,

[f] trityl = triphenylmethyl.

a much faster reaction ensued but with a longer induction period; for close comparison it proved desirable to work at 0.5 mol% catalyst, and then the normalised turnover rate differs by a factor of 4.5. At 5°C, the selectivity was superior, 96/4 in favour of the $2R^*,3R^*$ isomer of **16**. For comparison, similar reductions were carried out with the rhodium complex **19**, with closely comparable results. It is common observation that homogeneous Ru hydrogenations are more tolerant of substitution on the double bond than are Rh hydrogenations; a good example is the wide range of unsaturated carboxylic acids which can be successfully reduced in high enantiomeric excess using BINAPRu complexes[23]. In order to assess this, the hydrogenation of pure *E* or *Z* stereoisomers of dimethyl 2-ethylidene-3-methylbutanedioate **17** was carried out, using the ruthenium catalyst **12f** at 25°C under the conditions described above. The results were remarkably similar to those obtained by *Conn*[23] with the rhodium catalyst **19**; the *Z* isomer of **17** is reduced about four times slower than the *E* isomer and gives a 2:1 mixture of products in which the $2R^*,3R^*$-isomer is predominant. In contrast **(*E*)-17** is hydrogenated smoothly and give 97% of the $2R^*,3R^*$ diastereomer, identified by comparison with literature NMR data for authentic samples of the pure isomers[24]. This indicates that the substituent on the double bond prefers to be *syn* to the directing group, as in the inset [β] of Figure 2. A similar situation ensues in the asymmetric hydrogenation of dehydroamino acids, where the *Z* isomer is often more reactive, and reduced with higher enantioselectivity, than is the *E* isomer.

In two distinct cases the ruthenium complex **12** and the rhodium complex **19** behave very similarly in directed hydrogenation of allylic esters, implying mechanistic similarities. It is of some interest that the acac complex **12f** is much more reactive than the F_6acac complex **12a**, implying that the ancilliary ligand remains at least part-coordinated during the catalytic cycle. For both the Rh and the Ru catalyst, carboxylate rather than hydroxyl-binding in the alkene-bound chelate controls the stereochemical outcome of hydrogenation of reactant **15** giving predominantly R^*,R^*-**16**. For the trisubstituted alkene **17**, the *E* isomer hydrogenates more readily and more selectively than does the *Z* isomer in both series. This indicates

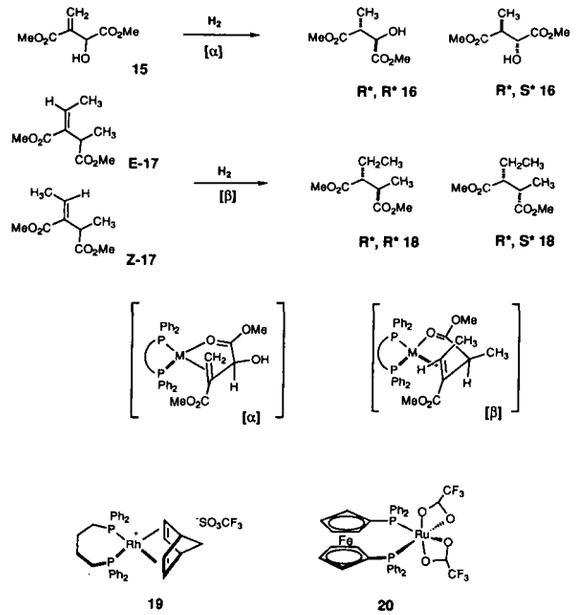


Figure 2. Directed hydrogenations with rhodium and ruthenium complexes; the inset structures [α] and [β] represent the preferred form of the coordinated alkene with chelated directing group.

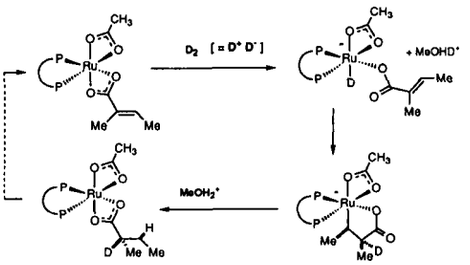


Figure 3. The heterolytic mechanism for hydrogenation of αβ-unsaturated acids with Ru-BINAP catalysts proposed by Ashby and Halpern.

coordinated intermediates which are common to both catalysts, with preferred structures indicated in Figure 2.

Deuteration studies

It was indicated in the Introduction that there have been very few serious mechanistic studies of ruthenium asymmetric hydrogenation. Even the mechanism of action of common $(PPh_3)_nRuCl$-type complexes in the reduction of simple alkenes[25] is less well understood than that by $(PPh_3)_3RhCl$[26]. Such insights as exist come largely from the hydrogenation of α,β-unsaturated carboxylic acids using D_2 in MeOH or H_2 in MeOD. This work demonstrates that one hydrogen comes from the catalyst and one from the solvent, and is consistent with the pathway shown in Figure 3. *Ashby* and *Halpern*, with kinetic evidence to support the proposed catalytic cycle, have suggested that the reaction follows an ionic pathway, with a formal hydride transfer in the first step. The product is then formed by protonolysis of the oxametallocyclic intermediate. The same outcome would be achieved if hydridic intermediates in the catalytic cycle were sufficiently long-lived to exchange labile protons with the solvent. A distinctive feature of *Halpern*'s polar mechanism is that one of the two hydrogens involved in the addition will be subject to isotopic exchange with the solvent, whilst the other will be delivered intact to the reactant. This is the case for the α,β-unsaturated acids involved in the earlier studies, but the generality has not been established, nor is the more mundane explanation of proton exchange in monohydridic intermediates challenged by existing the experimental evidence. For this reason, and with pure catalyst precursors of defined structure on hand, a study of deuterium incorporation was conducted with different reactants.

On the basis of previous work[27] in rhodium directed hydrogenation and kinetic resolution, two reactants **21** and **22** were selected for the study of deuterium incorporation with the new ruthenium catalysts. Hydrogenations were carried out either with D_2 and MeOH as solvent or H_2 and MeOD as solvent, at ambient pressure or in a Fischer Porter bottle at 30–60 psi initial pressure. Analysis of deuterium content was carried out by a combination of NMR and MS techniques as appropriate, including ^1H, ^2H, ^{13}C spectra and especially ^1H- and ^2H-decoupled ^{13}C spectra[28].

Reactions of the allylic alcohol **21** are summarised in Table 1. With the achiral ligand in complex **12f**, reductions were easily carried out to completion, and the expected stereoisomer from directed hydrogenation was obtained in > 95% *de* (diastereomeric excess); the *syn*-diastereomer was not detected. The pattern of deuteration was revealed by NMR, but was not at all like that expected on the basis of prior work. Taking first the results obtained with H_2 in MeOD, Entry 1 indicates that there

is significant exchange of solvent with the intermediates in the catalytic cycle, and the result indicates that one of the two new hydrogens in the product is in part drawn from MeOD, but with little positional selectivity. There is little dideuteration of the product. Changing the H_2 pressure from 15 psi to 60 psi (initial) had little effect. This result is confirmed by repeating hydrogenation under the same conditions with D_2 in MeOH (Entry 2). The total uptake of deuterium is significantly greater under the latter conditions, but the essential similarity between the two experiments is indicated by comparison of the ^{1}H- and ^{2}H-decoupled ^{13}C NMR spectra in the region of the C2-methyl carbon at 13.6 ppm (Figure 4), which separates all four isotopomers of product and shows that the two monodeuterated isotopomers are present in equal amount in both cases. When similar experiments with H_2 in MeOD (at 30 psi initial pressure) were carried out employing the BINAP complex **12g**, (Entry 3), comparable results were obtained, and again the two monodeuterated isotopomers were formed in comparable amounts. The reaction was carried out to ca. 50% completion so that the product reflects the "matched" catalyst substrate pair. An analogous result was obtained using the analogous racemic BINAP complex and carrying out the reduction to completion. For the alternative isotopic experiment using D_2 in MeOH, (Entry 4), the non-deuterated isotopomer is essentially absent but again the two possible monodeuterated species are present in comparable amount. This is reinforced by the observation of two peaks of similar intensity in the ^{2}H NMR spectrum at 2.4 and 1.1 ppm. In order to establish that the deuteration pathway was not an anomaly associated with the F_6acac catalysts, complex **20** was prepared by the *Heiser* route[8]. Hydrogenation was

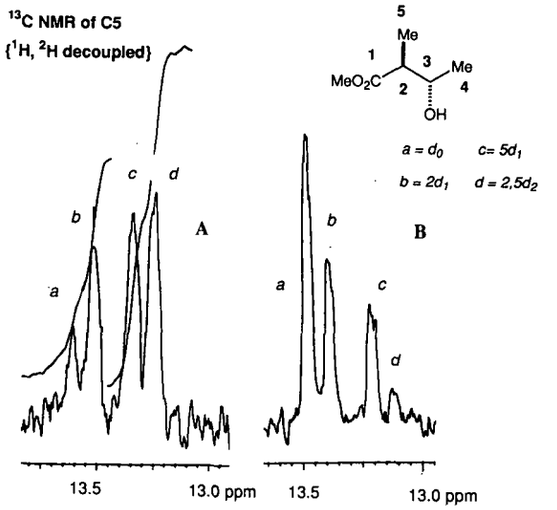
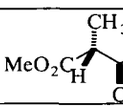
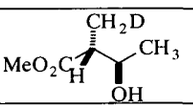
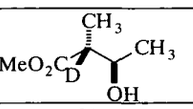
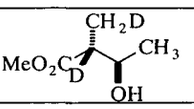


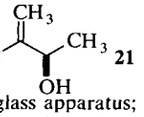
Figure 4. Proton- and deuterium-decoupled ^{13}C-NMR spectra of the reduction products from compound **21**, *carried out with* D_2 *in MeOH A and* H_2 *in MeOD B.*

carried out at 30 psi with H_2 in CD_3OD; the product distribution (Entry 5) was quite similar to that observed with the standard complexes of type **12**.

For the 2-methyl-3-methylenebutanedioic ester **22**, a simpler pattern emerged. When reaction was carried out with H_2 in MeOD using the achiral ligand complex **12f**, there was very little incorporation of deuterium (Table II, Entry 1). Correspondingly, with D_2 in MeOH, the main isotopomer was the dideuterated product, with a slight bias

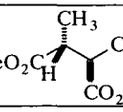
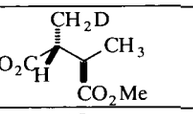
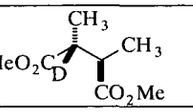
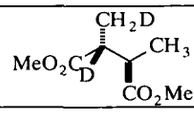
Table I Deuterium distribution in hydrogenations of compound **21** *under various conditions.*

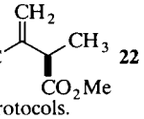
Entry	Conditions				
1	**12f**, H_2, MeOD	50	25	21	4
2	**12f**, D_2, MeOH	8	28	25	39
3	**12g**, H_2, MeOD, 30 psi	52	24	24	–
4	**12g**, D_2, MeOH, 30 psi	–	33	33	33
5	**20**, H_2, CD_3OD	30	35	35	< 5

From hydrogenation of  **21**

Reactions were carried out in glass apparatus; typically 9 mg (0.8 mol%) of catalyst precursor **12f** was mixed with 4 μl of $Me_3SiOSO_2CF_3$ *in* CH_2Cl_2 (1 ml.) and after brief standing solvent was removed in vacuo leaving an orange gum. This was dissolved in MeOH (2.5 ml.) containing 0.144 g of alkene and after rigorous degassing stirred under D_2 at 1 atm for 22 h. Solvent was removed *in vacuo* and the residue distilled (Kugelroh, 0.1 mmHg) giving 0.113 g (77%) of a colourless oil.

Table II Deuterium distributions in hydrogenation of compound **22** *under various conditions.*

Entry	Conditions				
1	**12f**, H_2, MeOD	90	< 5	< 5	–
2	**12f**, D_2, MeOH	–	10	10	80
3	**12g**, H_2, MeOD, 30 psi	80	10	10	–
4	**12g**, D_2, MeOH, 30 psi	15	15	25	45

From hydrogenation of  **22**

See Table I for experimental protocols.

towards the methyl group of the exchange-incorporated proton (Entry 2). In both cases the diastereoselectivity was better than 95%. Consistent observations were obtained with the BINAP complex **12g** as catalyst. A complication in accurate analysis of the latter data is that the reaction is no longer stereospecific, and significant amounts of the *meso* diastereomer of product are formed; especially when the hydrogenation is carried out to completion, employing the non-racemic ligand. The results fit the earlier trends (Entries 3, 4) although the presence of the second diastereomer (coupled to the internal symmetry of the product) makes the analysis more difficult, and hence more approximate. Nevertheless, the pattern of isotope incorporation (evenly distributed between the two positions of the reduced bond) is repeated.

Mechanism of hydrogenation

Two different types of experiment have been conducted with the ruthenium catalysts based on complex **12**. Firstly, they behave in directed hydrogenation experiments in a very similar way to cationic Rh diphosphine complexes, in terms of the stereoselectivity, the relative reactivity of different reactants and in discrimination between directing groups.. Secondly, there is a consistent pattern which has emerged from the isotopic labelling studies, different from that established for the Ru-BINAP reduction of unsaturated carboxylic acids. The basic feature is that both hydrogen atoms involved in the addition process undergo isotopic exchange with the hydroxyl group of solvent methanol, and to a similar extent. The simplest interpretation is that the exchange process precedes the transfer of hydrogen to the coordinated substrate, and that little occurs after the alkylruthenium(II)hydride intermediate is formed. Two different substrates which are hydrogenated at similar rates show very different degrees of isotope exchange, indicating that distinct intermediates are involved. The results are consistent with the catalytic cycle shown in Figure 5, where the primary point for isotopic exchange is Step A rather than Step B. It is implied that both the exchange and the hydrogen transfer are non-stereospecific and the kinetic isotope effect for H or D transfer is close to unity.

Although different reactants are involved here, these results do not lend support to the suggestion of *Halpern* and *Ashby* that ruthenium hydrogenation proceeds through an ionic mechanism in which the first step is a hydride transfer to the metal; its subsequent transfer to the substrate is then followed by protonolysis of the ensuing M C bond. In this case as well the results could be explained by a conventional exchange process, but at the alkylhydride step. Presumably the carboxylate group of the coordinated reactant (or from the acetate of the original catalyst) can assist in proton relay between ruthenium and solvent. Hence we currently favour a conventional stepwise process involving the initial addition of dihydrogen to form first an η^2 and then an η^1,η^1 dihydride. We prefer to defer a more detailed discussion of the mechanism until other experiments have been completed.

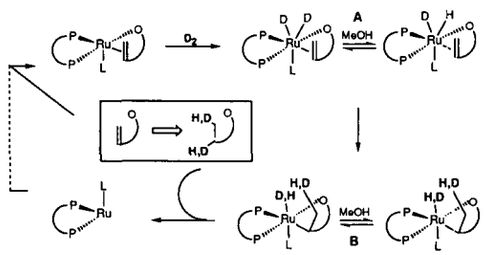


Figure 5. A mechanism for Ru hydrogenation which fits the available facts. In the cases reported here, the predominant exchange process is in step (a) whilst for the BINAP reductions of unsaturated acids reported in Ref. 4 and the predominant exchange takes place at step (b).

Experimental

General procedures

Reactions were carried out in solvents distilled from standard drying agents[29]. Reactions of compounds of an air sensitive nature were carried out under an argon atmosphere, using standard vacuum line techniques. Solvents were deoxygenated by the freeze-thaw cycle in which the solvent was first frozen in liquid N_2 and then warmed up *in vacuo* (0.1 mm Hg), and subsequently flushed with argon. The ruthenium catalyst precursor **20** was prepared following the method of *Heiser*[8,30].

Melting points were determined using a Reichert-Koffler block and are uncorrected.

^{1}H-NMR spectra were recorded on Varian Gemini 200 (200 MHz) and Bruker WA 500 (500 MHz) spectrometers. ^{13}C-NMR spectra were recorded on a Varian Gemini 200 (50.31 MHz) and Bruker WA 500 (125.6 MHz) spectrometer and chemical shifts quoted as δ parts per million (ppm) downfield of tetramethylsilane. ^{31}P-NMR spectra were recorded on a Bruker WA 250 (101.26 MHz) spectrometer, with chemical shifts quoted as δ parts per million downfield of 85% H_3PO_4. Abbreviations used in the description of NMR spectra are: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, qt = quartet of triplets, ABq = AB quartet, m = multiplet, br = broad, J = coupling constant, acac = acetylacetonate, fluoroacac = hexafluoroacetylacetonate, exch. = exchange.

Infrared spectra were recorded on a Perkin Elmer 1750 Fourier-Transform spectrometer either as a liquid film or as a KBr disk. Abbreviations used in the description of infrared spectra are: s = strong, m = medium, w = weak, br = broad.

Mass spectra were recorded on a V.G.Micromass, a V.G.Masslab and a V.G.Trio-1 spectrometer. Values are followed, in parentheses, by the intensity as a percentage of the base peak. GC conditions are as quoted in the text.

Elemental microanalyses were carried out by Mrs. *V. Lamburn* in the Dyson Perrins Laboratory.

(η^4-Bicyclo[2.2.1]hepta-2,5-dienyl)(η^3-prop-2-enyl)(1,1,1,5,5,5-hexafluoroacetylacetonato) ruthenium(II) (**11a**)

(η^4-Bicyclo[2.2.1]hepta-2,5-dienyl)(η^3-prop-2-enyl)(*bis* η^1-acetonitrilato)ruthenium(II)tetra-fluoroborate (**10a**, 0.650 g, 1.61 mmol) was dissolved in degassed acetone (10 ml). To this was added sodium 1,1,1,5,5,5-hexafluoroacetylacetonate (0.375 g, 1.63 mmol) in acetone (5 ml), and the solution stirred at room temperature for 12 h. The solvent was removed *in vacuo*, then the residue dissolved in dry, degassed hexane (10 ml) and filtered through 0.5 cm of celite. The solvent was again removed *in vacuo* to give a brown oil. Further purification by short-path distillation (100°C at 0.01–0.02 mmHg) gave **11a** as a red crystalline solid (0.411 g, 58%). Anal. calcd. for $C_{15}H_{14}F_6O_2Ru$ (441.33): C 40.8, H 3.2; found: C 40.9, H 3.1%. ^{1}H-NMR (500 MHz, C_6D_6); δ (C_7H_8): 3.93 (1H, t, $J \sim 4$ Hz, olefin), 3.80 (1H, t, $J \sim 4$ Hz, olefin), 3.56 (1H, t, $J \sim 4$ Hz, olefin), 3.42 (1H, m, methine), 3.04 (1H, br, s, methine), 1.34 (1H, t, $J \sim 4$ Hz, olefin), 1.1 (2H, ABq, methylene): propenyl; 4.3–4.6 (1H, m, 2-H), 3.51 (*E*) (1H, d, J 10 Hz, 3-H), 2.98 (*E*) (1H, d, J 7 Hz, 1-H), 2.48 (*Z*) (1H, d, J 10 Hz, 1-H), 1.63 (*Z*) (1H, d, J 13 Hz, 3-H): fluoroacac; 5.92 (1H, s, 3-H). ^{13}C-NMR (50.31 MHz, C_6D_6); δ (C_7H_8): 62.5 (olefin), 60.6 (olefin), 59.6 (olefin), 53.2 (olefin), 50.7 (methine), 46.9 (methine), 38.0 (methylene); propenyl: 89.6 (C2), 77.4, 57.6; fluoroacac: 111.4 (C3). IR (KBr) υ_{max}: 3008 (C = C-H), 2950 (CH), 2988 (CH), 2912 (CH), 2853 (CH), 1587 (C=C) cm^{-1}. MS (CI^+, NH_3) m/z (%; fragment): 442 (100, M+1,), 401 (30, M-propenyl), 193 (63, M-propenyl-facac). There was evidence in the NMR spectra of a minor isomer, ratio major/minor = 1.7/1, and peaks corresponding to this (not hidden by peaks of the major isomer) are as follows: ^{1}H-NMR (500 MHz, C_6D_6); δ (C_7H_8): 4.45 (2H, overlap, olefin), 3.51 (1H, overlap, olefin), 3.41 (1H, overlap, methine), 2.87 (1H, br, s, methine), 1.86 (1H, t, olefin), 1.08 (2H, ABq, methylene); propenyl: 3.75 (1H, m, overlap, 2-H), 2.57 (*Z*) (1H, d, J 10 Hz, 1-H), 2.39 (*E*) (1H, d, J 7 Hz, 1-H); fluoroacac: 6.09 (1H, s, 3-H). ^{13}C-NMR (50.31 MHz,

C_6D_6); δ (C_7H_8): 66.6 (olefin), 61.5 (olefin), 57.9 (olefin), 53.8 (olefin), 51.0 (methine), 48.5 (methine), 45.0 (t, methylene); propenyl: 79.5, 62.5, 111.4 (C2); fluoroacac: 128.3 (C3).

(η⁴-Cycloocta-1,5-dienyl)(η³prop-2-enyl)(1,1,1,5,5,5-hexafluoroacetylacetonato) ruthenium(II) (**11b**)

Following the above procedure, (η⁴-cycloocta-1,5-dienyl)(η³-prop-2-enyl)(*bis* η¹-acetonitrile) ruthenium(II) tetrafluoroborate (**10b**, 589 mg, 1.4 mmol) was reacted with sodium 1,1,1,5,5,5-hexafluoroacetylacetonate (332 mg, 1.4 mmol), to give an orange oil. Further purification by short-path distillation (150°C at 0.05 mmHg) gave **11b**, which crystallised on seeding (481 mg, 73%). Anal. calcd. for $C_{16}H_{18}F_6O_2Ru$ (457): C 42.0, H 3.9; found: C 42.0, H 3.9%. ^{1}H-NMR (500 MHz, CD_2Cl_2); δ (C_8H_{12}): 4.70 (1H, dd, *J* ~ 4 Hz, *J* 6 Hz and 9 Hz, olefin), 4.03 (1H, td*J* 8 Hz, olefin), 3.76 (1H, d, *J* 6.5 Hz, olefin), 3.50 (1H, dd, *J* 6 Hz and 9 Hz, olefin), 2.53–2.75 (3H, m,), 2.01–2.11 (2H, m), 1.68–1.76 (1H, m), 1.50–1.59 (1H, m); propenyl: 4.69 (1H, m, 2-H), 3.70 (1H, dd,*J* 15 Hz and 9 Hz), 2.83 (1H, d, *J* 11 Hz), 2.5 (1H, dd, *J* 15 Hz and 8 Hz), 1.95 (1H, dd, *J* 15 Hz and 8 Hz); fluoroacac: 5.91 (1H, s, 3-H). ^{13}C-NMR (125.6 MHz, CD_2Cl_2); δ (C_7H_8): 62.5 (olefin), 60.6 (olefin), 59.6 (olefin), 53.2 (olefin), 50.7 (methine), 46.9 (methine), 38.0 (methylene); propenyl: 89.6 (C2), 77.4, 57.6; fluoroacac: 176 and 173 (CF_3), 118 and 116 (C=O), 111.4 (C3). IR (KBr) υ_{max}: 3008 (C=C-H), 2950 (CH), 2988 (CH), 2912 (CH), 2853 (CH), 1587 (C=C) cm^{-1}. MS (CI^+, NH_3) *m/z* (%; fragment): 442 (100, M+1,), 401 (30, M-propenyl), 193 (63, M-propenyl-facac). There was again evidence in the NMR spectra of a minor isomer, ratio major/minor = 5/1, and peaks corresponding to this (not hidden by peaks of the major isomer) are as follows: ^{1}H-NMR (500 MHz, C_6D_6): δ propenyl; 4.98 (1H, m, 2-H), 3.87 (1H, m,), 2.38 (1H, d, *J* 4 Hz): fluoroacac; 5.77 (1H, s).

(η⁴-Bicyclo[2.2.1]hepta-2,5-dienyl)(η³-prop-2-enyl)(acetylacetonato)-ruthenium(II) (**11c**)

Following the procedure for **11a**, **10a** (0.747 g, 1.85 mmol) and sodium acetylacetonate (0.226 g, 1.85 mmol) were reacted together to give a brown oil. Short-path distillation of the oil (115°C at 0.04 mm.Hg) gave **11c** as a yellow crystalline solid (0.385g, 62%). ^{1}H-NMR (500 MHz, C_6D_6): δ (C_7H_8); 4.12 (1H, t, *J* 3.9 Hz, olefin), 3.92 (1H, t, *J* 3.9 Hz, olefin), 3.80 (1H, br, s, methine), 3.73 (1H, t, *J* 3.6 Hz, olefin), 3.32 (1H, br, s, methine), 1.59 (1H, t, *J* ~ 4 Hz, olefin), 1.31 (2H, ABq, methylene): propenyl; 4.6–4.9 (1H, m, 2-H), 3.61 (*E*) (1H, d, *J* 7.1 Hz, 3-H), 3.22 (*E*) (1H, d, *J* 6.1 Hz, 1-H), 2.65 (*Z*) (1H, d, *J* 7.6 Hz, 1-H), 1.82 (*Z*) (1H, d, *J* 12.6 Hz, 3-H): acac; 5.03 (1H, s, 3-H), 1.97 (3H, s), 1.52 (3H, s); ^{13}C-NMR (50.31 MHz, C_6D_6): δ (C_7H_8); 59.2 (olefin), 58.7 (olefin), 58.2 (olefin), 50.3 (olefin), 50.1 (methine), 47.1 (methine), 38.3 (methylene): propenyl; 99.2 (C2), 76.4, 57.1: acac; 104.5 (C3), 27.9, 27.2 (quaternary carbons not visible). υ_{max} (KBr) 2988 (CH), 2950 (CH), 2912 (CH), 2853 (CH), 1587 (C=O), 1517 (C=C) cm^{-1}.
Again, the NMR spectra also showed a minor isomer, ratio major/minor = 4/1, and visible peaks corresponding to this are as follows: ^{1}H-NMR (500 MHz, C_6D_6): δ (C_7H_8): 4.86 (2H, t, *J* 4.9 Hz, olefin), 4.75 (1H, t, *J* 1.9 Hz, olefin), 3.99 (1H, br, s, methine), 3.14 (1H, br, s, methine), 1.05 (2H, ABq, methylene): propenyl; 4.63 (1H, m, 2-H), 2.85 (1H, br, s), 2.78 (1H, br, s): acac; 5.19 (1H, s, 3-H), 1.52 (3H, s), 2.12 (3H, s). ^{13}C-NMR (50.31 MHz, C_6D_6): δ (C_7H_8); 57.8 (olefin), 50.9 (olefin), 49.8 (methine), 49.5 (methine): propenyl; 78.5 (C).

*[1,1'-*Bis*(diphenylphosphino)ferrocene](η³-prop-2-enyl)(1,1,1,5,5,5-hexafluoro-acetylacetonato)ruthenium(II)* (**12a**)

10b (110 mg, 0.24 mmol) was degassed in a Schlenk tube and dissolved in dry, degassed THF (5 ml). 1,1'-Bis(diphenylphosphino) ferrocene (133.6 mg, 0.24 mmol) in THF (5 ml) was added whilst stirring and the solution was refluxed for 5 h, until the colour had changed to dark brown. The solvent was removed *in vacuo* and the remaining solid washed repeatedly with dry, degassed hexane. Recrystallisation from a 1/1 mixture of CH_2Cl_2 and hexane gave **12a** as brown crystals (159.7 mg, 85%); m.p. 153°C. Anal. calcd. for $C_{42}H_{34}F_6FeO_2P_2Ru$ (903): C 55.8, H 3.8; found: C 55.5, H 3.8%. ^{1}H-NMR (500 MHz, CD_2Cl_2); δ (DPPF): 7.2–7.9 (20H, m, aromatic), 5.55 (1H, br, s), 5.32 (1H, br, s), 5.31 (1H, br, s), 4.69 (1H, br, s), 4.39 (1H, br, s), 4.17 (1H, br, s), 4.07 (1H, br, s), 3.65 (1H, br, s); propenyl: 4.25 (1H, m, 2-H), 2.53 (*E*) (1H, d, *J* 5.2 Hz, 3-H), 1.94 (*E*) (1H, t, *J* 4.6 Hz, 1-H), 1.19 (*Z*) (1H, m, 1-H), 0.95 (*Z*) (1H, d, *J* 10.4 Hz, 3-H): fluoroacac: 5.39 (1H, s, 3-H): ^{13}C-NMR (50.31 MHz, CD_2Cl_2); δ (DPPF): 127.3–135.8 (aromatic), 76.9, 77.1, 74.2, 74.0, 72.9, 72.8, 70.38, 69.87; propenyl: 54.5, 55.7, 90.22 (C2); fluoroacac: 164.2, 156.0, 93.31 (C3). ^{31}P-NMR (101.26 MHz, THF): δ 62.2 (d, *J* 34.3 Hz), 28.3 (d, *J* 34.2 Hz). IR (KBr) υ_{max}: 1613 (C=O), 1541 (C=C) cm^{-1}.

*[1,1'-*Bis*(diphenylphosphino)ferrocene](η³-prop-2-enyl)(acetylacetonato)ruthenium(II)* (**12f**)

Following the above procedure, **10a** (0.030 g, 0.090 mmol) and 1,1'-bis-(diphenylphosphino)ferrocene (0.050 g, 0.090 mmol) were reacted together to produce **12f** as a yellow crystalline solid, (0.038 g, 53%), m.p. 193–195°C. ^{1}H-NMR (500 MHz, CD_2Cl_2); δ (DPPF): 7.2–7.9 (20H, m, aromatic), 5.89 (1H, br, s), 4.58 (1H, br, s), 4.40 (1H, br, s), 4.09 (3H, br, s), 3.78 (1H, br, s), 3.66 (1H, br, s); propenyl: 4.0–4.2 (1H, m, 2-H), 2.23 (*E*) (1H, d, *J* 5.6 Hz, 3-H), 1.64 (*E*) (1H, t, *J* 5.0 Hz, 1-H), 1.09 (*Z*) (2H, m, 1-H), 0.70 (*Z*) (1H, d, *J* 10.4 Hz, 3-H); acac: 4.89 (1H, s, 3-H), 1.99 (3H, s), 1.361 (3H, s). ^{13}C-NMR (50.31 MHz, CD_2Cl_2); δ (DPPF): 127–135 (aromatic), 91.24, 77.03, 74.41, 74.23, 74.03, 73.87, 72.18, 69.9; propenyl: 69.29 (C2), 53.79, 52.58; acac: 99.17 (C3), 28.05, 27.84 (quaternary carbons not visible). ^{31}P-NMR (101.26 MHz, THF); δ 63.4 (d, *J* 35.6 Hz), 27.8 (d, *J* 35.5 Hz). IR (KBr) υ_{max}: 2988 (CH), 1579 (C=O), 1507 (C=C) cm^{-1}.

*[1,4-*Bis*(diphenylphosphino)ethano](1,1,1,5,5,5-hexafluoroacetylacetonato)ruthenium(II)* (**12b**)

10b (101.9 mg, 0.22 mmol) in dry, degassed THF (2 ml) was added to 1,4-bis(diphenylphosphino)ethane (73.4 mg, 0.18 mmol) in THF (2 ml). The solution was refluxed for 24 h. The solvent was removed *in vacuo* and the residue adsorbed onto Al_2O_3 and washed repeatedly with dry, degassed hexane and then eluted with MeOH to give **12b** (81.3 mg, 60%), m.p. 58°C. Anal. calcd. for $C_{34}H_{30}F_6O_2P_2Ru$ (747): C 54.6, H 4.0; found: C 54.6 H 3.9%. ^{31}P-NMR (101.26 MHz, THF): δ 90.9 (d, *J* 26 Hz), 63.3 (d, *J* 26 Hz).

*(S)-[2,2'-*Bis*(diphenylphosphino)-1,1'-binaphthalene](η³-prop-2-enyl)-(1,1,1,5,5,5-hexafluoroacetylacetonato)ruthenium(II)* (**12c**)

10b (111.4 mg, 0.24 mmol) in dry, degassed toluene (2 ml) was added to (S)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene (BINAP) (122.6 mg, 0.20 mmol) in toluene (3 ml). The solution was refluxed for 24 h. The solvent was removed *in vacuo*, and the residue washed repeatedly with dry, degassed hexane until the solvent which was being filtered off became colourless. This produced **12c** as a pale brown solid (149.6 mg, 77%), m.p. 247–248°C. Anal. calcd. for $C_{52}H_{38}F_6O_2P_2Ru$ (971): C 64.25, H 3.9; found: C 63.9, H 4.1%. ^{1}H-NMR (500 MHz, CD_2Cl_2); δ (BINAP): 6.1–8.2 (32H, m); propenyl: 4.37 (1H, m, 2-H), 3.31 (1H, d, *J* 6 Hz), 2.38 (1H, m), 1.14 (1H, dd, *J* 6.5 Hz and 11.5 Hz), 0.74 (1H, d, *J* 11 Hz); fluoroacac: 5.86 (1H, s). Again, the NMR spectra also showed a minor isomer, ratio major/minor = 3/1, and visible peaks corresponding to this are as follows: ^{1}H-NMR (500 MHz, CD_2Cl_2); δ propenyl: 4.6 (1H, m, 2-H), 3.57 (1H, m), 1.65 (1H, dd, *J* 6 Hz and 11.5 Hz); facac: 5.49 (1H, s). ^{31}P-NMR (101.26 MHz, THF); δ (major isomer): 64.9 (d, *J* 38 Hz), 34.7 (d, *J* 38 Hz); (minor isomer): 59.9 (d, *J* 43 Hz), 31.3 (d, *J* 43 Hz).

*(S)-[2,2'-*Bis*(diphenylphosphino)-1,1-binaphthalene](η³-prop-2-enyl)-(acetylacetonato)ruthenium(II)* (**12g**)

The above procedure was followed using **10a** (20 mg, 0.06 mmol) and (S)-(BINAP) (37 mg, 0.06 mmol). This gave **12g** as a brown solid (20 mg, 39%); m.p. 253–258°C. ^{1}H-NMR (500 MHz, $CDCl_3$); δ (BINAP); 6.1–8.4 (32H, m); propenyl: 4.65–4.75 (1H, m, 2-H), 3.45 (1H, d, *J* 7.1 Hz), 2.68 (1H, t, *J* 5.1 Hz), 1.67–1.72 (1H, m), 1.36 (1H, d, *J* 10.5 Hz); acac: 5.25 (1H, s), 2.12 (3H, s), 1.27 (3H, s). δ_P(101.26MHz, THF); δ (major isomer): 65.0 (d, *J* 37 Hz), 37.3 (d, *J* 7.1 Hz); (minor isomer): 64 (d, *J* ~ 40 Hz), 36 (J ~ 40 Hz). (quantity of minor isomer too small to be seen in ^{1}H-NMR).

*(−)-[2,3-O-Isopropylidene-1,4-*bis*(diphenylphosphino)butane-2,3-diol](η³-prop-2-enyl)(1,1,1,5,5,5-hexafluoroacetylacetonato)ruthenium-(II)* (**12d**)

10b (87.1 mg, 0.19 mmol) in dry, degassed THF (2 ml) was added to (−)-2,3-O-isopropylidene-1,4-bis(diphenylphosphino)butane-2,3-diol (79.2 mg, 0.16 mmol) in THF (2 ml). The solution was refluxed for 24 h. The solvent was removed *in vacuo* and the residue adsorbed onto SiO_2 and washed repeatedly with dry, degassed hexane, then eluted through with Et_2O. The solvent was then again removed *in vacuo* and the residue dissolved in MeOH and filtered through Al_2O_3. Finally, the residue was filtered through celite with Et_2O and the solvent removed to give **12d** (81.2 mg, 60%), m.p. 75°C. Anal. calcd.

for $C_{39}H_{38}F_6O_4P_2Ru$ (847): C 55.3, H 4.5; found: C 55.4, H 4.7%. ^{1}H-NMR (500 MHz, CD_2Cl_2); δ (only facac and propenyl resonances shown); propenyl: 4.05–4.11 (1H, m, 2-H), 2.25 (1H, dd, *J* 10 Hz and 14 Hz), 1.15 (1H, dd), 0.88 (1H, d); fluoroacac: 5.88 (1H, s). ^{31}P-NMR (101.26 MHz, THF); δ (major isomer): 58.0 (d, *J* 40 Hz), 15.7 (d, *J* 40 Hz); (minor isomer): 48.9 (d, *J* 40 Hz), 19.1 (d, *J* 40 Hz).

*(−)-[1,2-*Bis*[(diphenylphosphino)-methyl]-3,4-dimethylcyclobutane]-(η^3-prop-2-enyl)(1,1,1,5,5,5-hexafluoroacetylacetonato)ruthenium(II)* (**12e**)

10b (101.9 mg, 0.22 mmol) in dry, degassed THF (2 ml) was added to (−)-1,2-bis[(diphenylphosphino)-methyl]-3,4-dimethylcyclobutane (82.6 mg, 0.18 mmol) in THF (2 ml). The solution was refluxed for 24 h. The solvent was removed *in vacuo* and the residue washed repeatedly with dry, degassed hexane to give **12e** (81.2 mg, 60%), m.p. 95–96°C. Anal. calcd. for $C_{38}H_{36}F_6O_2P_2Ru$ (801): C 56.9, H 4.5; found: C 57.1 H 4.5%. ^{1}H-NMR (500 MHz, CD_2Cl_2); δ (only facac and propenyl resonances shown); propenyl: 3.99 (1H, m, 2-H), 3.10 (1H, *ddd*, *J* 4 Hz, 7.5 Hz and 16 Hz), 1.05 (1H, dd, *J* 6.5 Hz and 11 Hz), 0.68 (1H, d, *J* 10.5 Hz); fluoroacac: 5.82 (1H, s). Again, the NMR spectra also showed a minor isomer and visible peaks corresponding to this are as follows: ^{1}H-NMR (500 MHz, CD_2Cl_2); δ propenyl: 4.08 (1H, m, 2-H), 0.51 (1H, dd, *J* 11 Hz); facac: 6.00 (1H, s). ^{31}P-NMR (101.26 MHz, THF); δ (major isomer): 62.5 (d, *J* 37 Hz), 20.1 (d, *J* 37 Hz); (minor isomer): 51.8 (d, *J* 38 Hz), 24.1 (d, *J* 38 Hz).

Dimethyl 2-(diethylphosphynyloxy)-3-methylbutanedioate

Sodium hydride (*60% dispersion in mineral oil, 3.00 g, 75.0 mmol*) was washed twice with dry hexane and any traces of solvent remaining were then removed *in vacuo*. Dry 1,2-dimethoxyethane (50 ml) was added to give a suspension, then methyl diethylphosphonate (13.8 ml, 75.0 mmol) in 1,2-dimethoxyethane (20 ml) was added dropwise over a period of 1 h. Further stirring at room temperature under argon was carried out until no more effervescence occurred. Methyl 2-bromopropanoate (8.35 ml, 75 mmol) in glyme (10 ml) was added dropwise to the solution over 1 h, and the resulting solution stirred at room temperature for 1 h under argon. The sodium bromide precipitate was removed by centrifugation and the solvent removed (from the decanted solution) *in vacuo*, to give a yellow oil. Further purification by short-path distillation (173°C at 0.01 mmHg) gave dimethyl 2-(diethylphosphynyloxy)-3-methylbutanedioate as a colourless oil, which was shown by ^{1}H and ^{13}C-NMR to be a mixture of diastereomers, (17.3 g, 79%). ^{1}H-NMR (200 MHz, $CDCl_3$); δ 3.98–4.20 (4H, m, CH_2CH_3), 3.69 (3/2H, s, CO_2CH_3), 3.67 (3/2H, s, CO_2CH_3), 3.65 (3/2H, s, CO_2CH_3), 3.62 (3/2H, s, CO_2CH_3), 1.1–1.4 (6H, m, CH_2CH_3), 3.18–3.54 (1H, m, P-CH), 3.05 (1H, qt, *J* 7.7 Hz), 1.22–1.42 (3H, overlap, CH_3). ^{13}C-NMR (50.31MHz, $CDCl_3$); δ (major isomer): 175.51 (CO_2CH_3), 169.65 (CO_2CH_3), 62.93 ($CO_2CH_2CH_3$), 52.13 ($CO_2CH_2CH_3$), 49.48 (P-CH), 46.86, 16.14, 16.02 (CO_2CH_3), 15.90 (CO_2CH_3); (minor isomer): 175.14 (CO_2CH_3), 168.42 (CO_2CH_3), 62.82 ($CO_2CH_2CH_3$), 52.50 ($CO_2CH_2CH_3$), 48.89 (P-CH), 46.2, 15.58 (CO_2CH_3), 15.36 (CO_2CH_3). IR (film) ν_{max}: 2986 (CH), 2955 (CH), 2912 (CH), 1736 (C=O), 1438 (C=C), 1255 (P=O) cm^{-1}.

Dimethyl (Z)- and (E)-2-ethylidene-3-methylbutanedioate (**17**)

[This experiment was first carried out by Dr. *A. Conn* (D. Phil. Thesis, Oxford, 1991]. Dimethyl 2-(diethylphosphinato)-3-methylbutanedioate (17.3 g, 59.0 mmol) was dissolved in dry THF (20 ml) under an argon atmosphere, and cooled in an ice bath. NaH (60% dispersion in mineral oil, 2.40 g, 60.0 mmol) was added over a period of 30 min and the solution stirred at room temperature for 1 h. Acetaldehyde (6.90 ml, 147 mmol, 2.5 equiv.) was dissolved in dry THF (20 ml) and added dropwise to the first solution over a period of 1 h, which was then stirred at room temperature for 12 h. The solution was then added to a mixture containing Et_2O (100 ml) and distilled water (150 ml) and the aqueous layer extracted with portions of Et_2O (2×100 ml). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed *in vacuo* to give a yellow oil. Short-path distillation (87°C at 0.01 mmHg) gave (E)-**17** and (Z)-**17** as a colourless oil, (7.51 g, 69%). This was shown by NMR to contain a 1.6/1 mixture of *Z* and *E* geometrical isomers respectively, and these were separated by preparative GLC on a PEG 20 M column. *E* isomer: Anal. calcd. for $C_9H_{14}O_4$: C 58.5, H 7.9; found: C 58.0, H 7.6%. ^{1}H-NMR (200 MHz, $CDCl_3$); d 6.95 (1H, q, *J* 7.2 Hz, 2'-H), 3.74 (3H, s, -CO_2Me), 3.68 (3H, s, -CO_2Me), 3.48 (1H, q, *J* 7.2 Hz, 3-H), 1.85 (3H, d, *J* 7.2 Hz, 2''-H), 1.35 (3H, d, *J* 7.2 Hz, 3'-H). ^{13}C-NMR (50.31MHz, $CDCl_3$); δ 174.45 (CO_2CH_3), 167.07 (CO_2CH_3), 138.97 (C2'), 133.33 (C2), 51.91 (CO_2CH_3), 51.68 (CO_2CH_3), 37.21 (C3), 15.34 (C2''), 13.99 (C3'). IR (film) ν_{max}: 2984 (CH), 2953 (CH), 1746 (C=O), 1714 (C=O), 1650 (C=C). *Z* isomer: Anal. calcd. for $C_9H_{14}O_4$: C 57.7, H 7.6; found: C 58.0, H 7.6%. ^{1}H-NMR (200MHz, $CDCl_3$); δ 6.18 (1H, q, *J* 7.2 Hz, 2'-H), 3.76 (3H, s, -CO_2Me), 3.69 (3H, s, -CO_2Me), 3.48 (1H, q, *J* 7.4 Hz, 3-H), 2.06 (3H, d, *J* 7.4 Hz, 2''-H), 1.35 (3H, d, *J* 7.2 Hz, 3'-H). ^{13}C-NMR (50.31 MHz, $CDCl_3$); δ 174.78 (CO_2CH_3), 167.40 (CO_2CH_3), 138.83 (C2'), 132.09 (C2), 51.73 (CO_2CH_3), 51.13 (CO_2CH_3), 43.23 (C3), 16.24 (C2''), 15.54 (C3'). IR (KBr) ν_{max}: 2982 (CH), 2953 (CH), 1793 (C=O), 1741 (C=O), 1649 (C=C). MS (CI$^+$, NH_3) *m/z* (%; fragment): 187 (M+1, 25%), 155 (M-OMe, 55%), 127 (M-CO_2Me, 45%), 95 (100%).

Ethyl oxoacetate[31]

Diethyl tartrate (20.6 g, 0.10 mmol) was dissolved in dry Et_2O (200 ml) and the solution cooled in an ice/water bath. Periodic acid (22.8 g, 0.10 mol) was added in portions over 1 h whilst stirring the solution under argon. The stirring was continued until the cloudiness of the solution had virtually disappeared and a white solid had formed at the bottom of the flask, then the Et_2O phase was decanted off. The solution was dried over 4 Å molecular sieves for 30 min and the solvent removed *in vacuo*. The resulting oil was then distilled through a 10 cm Vigreux column (40–45°C at 21 mmHg) to give ethyl glyoxylate as a clear orange/yellow oil. The ^{1}H-NMR, mass spectrum, and infrared spectra all showed that the aldehyde polymerizes immediately, but the literature preparation notes that this is reversible and hence further reactions are possible.

1-ethyl 4-methyl 2-hydroxy 3-methylenebutanedioate[32] (**15**)

Methyl propenoate (1.49 g, 17.3 mmol) and ethyl oxoacetate (1.49 g, 17.3 mmol) were placed in a Schlenk tube, and 1,4-diazabicyclo[2.2.2]octane (0.388 g, 3.46 mmol) was added to the soluion as a catalyst. The mixture was stirred at 50°C for 12 h. Any unreacted starting material was removed *in vacuo* and further purification by short-path distillation (70°C at 0.01 mmHg) gave **15** as a yellow/orange oil, (2.60 g, 80%). Anal. calcd. for $C_8H_{12}O_5$: C 48.2, H 6.2; found: C 51.1, H 6.4%. ^{1}H-NMR (200 MHz, $CDCl_3$); δ 6.38 (1H, s, CH=CH_2), 5.95 (1H, s, CH=CH_2), 4.86 (1H, s, C*H*OH), 4.26 (2H, q, *J* 7.1 Hz, $CO_2CH_2CH_3$), 3.79 (3H, s, -CO_2Me), 1.27 (3H, t, *J* 7.1 Hz CO_2CH_{2CH3}). ^{13}C-NMR (50.31MHz, $CDCl_3$); δ 172.07 (CO_2Me), 165.98 (CO_2Et), 139.27 (C3), 127.86 (C=CH_2), 70.66 (C3), 61.39 ($CO_2CH_2CH_3$), 51.91 (CO_2CH_3), 13.26 ($CO_2CH_2CH_3$). IR (film) ν_{max}: 2984 (CH), 2957 (CH), 1733 (C=O), 1636 (C=C). MS (CI$^+$, NH_3) *m/z* (%; fragment); 189 (M+1, 100%), 206 (M+18, 30%).

Pd / C hydrogenation of **15**

5% Pd/C (0.131g) and **15** (0.331 g, 1.76 mmol) were placed in a Schlenk tube with MeOH (30 ml). The solution was degassed with argon thoroughly by three freeze-thaw cycles; and then with H_2 (by evacuating until the solution bubbled and then flushing with H_2, repeatedly 6 times at room temperature). A suitable pressure of H_2 was left above the solution, which was at 25°C, and the H_2 uptake followed by means of a burette. After 1 equivalent of H_2 had reacted, the solution was degassed by evacuating and flushing with argon, and filtered through a plug of celite. Further purification by short-path distillation (50°C, 0.01 mm Hg) gave **16** as a clear oil, (0.196 g, 59%). Two diastereomers, (*2R*,3S**) and (*2R*,3R**), of **16** were produced in a ratio of 3/2, and these were separated by preparative GLC at 150°C on an OV 225 column. ^{1}H-NMR (500 MHz, $CDCl_3$); δ (*2R*,3S**): 4.19–4.31 (3H, m, $CO_2CH_2CH_3$ and CO_2Et-C*H*), 3.69 (3H, s, CO_2CH_3), 3.06 (1H, d, *J* 5.4 Hz, OH, exch. with D_2O), 2.99–3.05 (1H, dq, *J* 3.7 Hz and 7.2 Hz, MeO_2C-C*H*), 1.29 (3H, d, *J* 7.0 Hz, $CO_2CH_2CH_3$), 1.28 (3H, t, *J* 7.2 Hz, CH-CH_3); (*2R*,3R**): 4.57 (1H, dd, *J* 3.6 Hz and 6.3 Hz, C*H*OH, but becomes d, *J* 3.6 Hz, on exch. with D_2O), 3.73 (3H, s, CO_2CH_3), 3.15 (1H, d, *J* 6.3 Hz, OH, exch. with D_2O), 2.93 (1H, dq, *J* 3.7 Hz and 7.1 Hz, MeO_2C-C*H*), 1.30 (3H, t, *J* 7.1 Hz, $CO_2CH_2CH_3$), 1.17 (3H, d, *J* 7.2 Hz, CHCH_3). ^{13}C-NMR (50.31 MHz, $CDCl_3$); δ (*2R*,3S**): 72.29 (*C*HOH), 61.97 ($CO_2CH_2CH_3$), 51.91 (CO_2CH_3), 43.08 (*C*HCH$_3$), 13.96 ($CO_2CH_2CH_3$), 12.75 (CH*C*H$_3$); (*2R*,3R**): 71.27 (*C*HOH), 62.13 ($CO_2CH_2CH_3$), 52.13 (CO_2CH_3), 42.90 (*C*HCH$_3$), 14.01 ($CO_2CH_2CH_3$), 10.39 (CH*C*H$_3$) (quaternary carbons not visible). IR (film) ν_{max}: (*2R*,3S**): 3436 (OH), 2920 (CH), 1734 (C=O), 1458 (CH), 1215 (C–O); (*2R*,3R**): 3437 (OH), 2919 (CH), 1736 (C=O), 1458 (CH), 1210 (C–O). MS (CI$^+$/NH_3) *m/z*

(%; fragment): 208 (30, M+18), 191 (100, M+1), 176 (10, M-CH_2), 159 (15, M-OMe). Retention time on capillary GC on an FFAP column at 165°C, *2R*,3S** and *2R*,3R** was 7.4 and 8.6 min respectively (ratio of isomers = 3/2 respectively).
The stereochemistry of the two sets of isomers was assigned by comparison with the literature ^{1}H-NMR resonances:

Reference	CH_3CH_2	CH_3CH	CH_3CH_2	2-H	3-H	CO_2CH_3
*2R*2S**	0.89, t *J* 7.2 Hz	1.10, d *J* 7.0 Hz	1.2–1.8, m	2.4–2.7, m		3.66, s
*2R*2S**	0.88, t	1.09, d	1.51, m	2.56, m		3.64, s
*2R*3R**	0.87, t	1.12, d	1.58, dq	2.59, dq	2.69, dt	3.63, s

*(η^4-bicyclo[2.2.1]hepta-2,5-dienyl)[1,4-*bis*(diphenylphosphino)butane]rhodium trifluoromethanesulphonate reduction of* **15**

15 (37.6 mg, 0.2 mmol) was placed in a Schlenk tube and degassed, then dry, degassed MeOH (0.5 ml) was added. $(C_7H_8)(Ph_2P-(CH_2)_4-PPh_2)Rh(CF_3SO_3)$ (3.65 mg, 0.006 mmol, 3 mol%) was also degassed in a Schlenk tube and then dissolved in MeOH (0.5 ml). Both solutions were placed, via a syringe, into a constant-volume vessel. The solution was degassed at −78°C three times with argon and six times with H_2 (the latter of the two activating the catalyst). Once a suitable, constant H_2 pressure had been obtained above the reaction solution, agitation of the solution by a stirrer was initiated. The uptake of H_2 was monitored by means of a pressure transducer and after 1 equivalent of H_2 had reacted, the solvent was removed *in vacuo* to an orange oil. Purification by vacuum distillation onto a cold trap and bucket gave **16** as a colourless oil, which contained mainly the *threo*-(*2R*,3S**) isomer. Both isomers were identified by comparison of the ^{1}H- and ^{13}C-NMR and capillary GC retention time with those for the Pd/C reduction products and the selectivity was measured by capillary GC at 165°C on an FFAP column.

Substrate	Temperature	Time	Selectivity 2R*,3R*/2R*,3S*	Yield of **16**
(15)	5°C	8 h	97/3	0.024 g, 63%
(15)	30°C	2 h	92/8	0.027 g, 68%

*[1,1'-*Bis*(diphenylphosphino)ferrocene](η^3-prop-2-enyl)(acetylacetonato)ruthenium(II) reduction of* **15**

15 (37.6 mg, 0.2 mmol) was degassed in a Schlenk tube and then dissolved in MeOH (0.5 ml). [1,1'-Bis(diphenylphosphino)ferrocene]-(η^3-prop-2-enyl)(acetylacetonato)ruthenium(II) (4.70 mg, 0.006 mmol, 3 mol%) was also degassed in a Schlenk tube and dissolved in CH_2Cl_2 (0.5 ml) Trimethylsilyl trifluoromethanesulphonate (23.2 μl of a 10% solution in CH_2Cl_2, 0.012 mmol, 2 equiv.) was added to the latter, and a colour change from yellow to green was noted. After a period of standing of 15 min, the solvent was removed *in vacuo* and replaced with dry, degassed MeOH (0.5 ml). The hydrogenations and work-ups were carried out as in the previous experiment, and the product stereochemistries determined by comparison with data for the Pd/C reduction products. The selectivity was again measured by capillary GC on an FFAP column.

Substrate	Temperature	Time	Selectivity 2R*,3R*/2R*,3S*	Yield of (**16**)
(15)	5°C	10 h	96/4	0.025 g, 65%
(15)	30°C	2 h	94/6	0.023 g, 61%

*[1,1'-*bis*(diphenylphosphino)ferrocene](η^3-prop-2-enyl)(1,1,1,5,5,5-hexafluoroacetylacetonato)ruthenium(II) reduction of* **15**

As described previously, **15** (37.6 mg, 0.2 mmol) was dissolved in MeOH (0.5 ml). [1,1'-bis(diphenylphosphino)ferrocene](η^3-prop-2-enyl)(1,1,1,5,5,5-hexafluoroacetylacetonato)ruthenium(II) (5.35 mg, 0.006 mmol, 3 mol%) was dissolved in CH_2Cl_2 (0.5 ml), trimethylsilyl trifluoromethanesulphonate (23.2 μl of a 10% solution in CH_2Cl_2, 0.012 mmol, 2 equiv.) was added and a colour change from purple/brown to red/orange was noted. After a period of standing of 15 min, the solvent was removed *in vacuo* and replaced with dry, degassed MeOH (0.5 ml). The hydrogenation was carried out as described above.

*[1,1'-*bis*(diphenylphosphino)ferrocene](η^3-prop-2-enyl)(acetylacetonato)ruthenium(II) reduction of* (E)- *and* (Z)-**17**

The above procedure was carried out using dimethyl (*Z*)- or (*E*)-**17** (37.2 mg, 0.2 mmol). This gave a colourless oil which contained **18** as the major product. ^{1}H-NMR (500 MHz, $CDCl_3$); d (*2R*,3R**); 3.69 (3H, s, -CO_2CH_3), 3.68 (3H, s, -CO_2CH_3), 2.81 (1H, dq, *J* 8.5 Hz and 7.2 Hz, 3-H), 2.65 (1H, dt, *J* 8.4 Hz and 4.8 Hz, 2-H), 1.6–1.7 (2H, m, CH_3CH_2-), 1.18 (3H, d, *J* 7.2 Hz, CH_3-CH), 0.89 (3H, t, *J* 7.4 Hz, CH_3CH_2-); (*2R*,3S**): 3.70 (3H, s, -CO_2CH_3), 3.69 (3H, s, -CO_2CH_3), 2.76 (1H, dq, *J* 7.5 Hz and 6.9 Hz, 3-H), 2.63 (1H, dt, *J* 7.6 Hz and 5.4 Hz, 2-H), 1.4–1.6 (2H, m, CH_3CH_2-), 1.14 (3H, d, *J* 6.9 Hz, CH_3-), 0.89 (3H, t, *J* 7.4 Hz, CH_3CH_2-). ^{13}C-NMR (50.31 MHz, $CDCl_3$); d (*2R*,3R**): 176.17 (-CO_2CH_3), 51.80 (-CO_2CH_3), 51.59 (-CO_2CH_3), 48.68 (C3), 40.30 (C2), 21.60 (-CH_3), 14.13 (-CH_2CH_3), 10.97 (-CH_2CH_3); (*2R*,3S**): 172.5 (-CO_2CH_3), 52.6 (-CO_2CH_3), 51.5 (-CO_2CH_3), 50.12 (C3), 41.75 (C2), 23.71 (-CH_3), 15.00 (-CH_2CH_3), 11.70 (-CH_2CH_3). MS (CI^+/NH_3) *m/z* (%, fragment): 189 (100, M+1), 157 (40, M-OMe). Retention time on capillary GC on an FFAP column at 100°C, *2R*,3R** and *2R*,3S** was 21.5 and 17.2 min, respectively.
The two diastereotopic sets of enantiomers were assigned by comparison with literature ^{1}H and ^{13}C-NMR data of dimethyl and diethyl ester analogues[25].

Substrate	Time	Temperature	Diastereoselectivity 2R*,3R*/2R*,3S*	Yield of **18**
(Z)-**17**	5 h	30°C	76/24	0.025 g, 68%
(E)-**17**	not measured	25°C	97/3	0.019 g, 52%

*Activation of [1,1'*bis*(diphenylphosphino)ferrocene](η^3-prop-2-enyl)-(1,1,1,5,5,5-hexafluoroacetylacetonato)ruthenium(II)*

[1,1'Bis(diphenylphosphino)ferrocene](η^3-prop-2-enyl)(1,1,1,5,5,5-hexafluoroacetylacetonato)ruthenium(II) (2.7 mg, 0.003 mmol) was dissolved in degassed CH_2Cl_2 (1 ml). Trimethylsilyl trifluoromethanesulphonate (0.006 mmol, 2 equiv.) was added and a colour change from purple/brown to red/orange was noted. After a period of 20 min standing, the solvent was removed *in vacuo* and replaced with dry, degassed MeOH (2 ml). This solution was then immediately injected into the electrospray MS and analysed. Repeating the experiment with a 10-fold excess of trimethylsilyl trifluoromethanesulphonate gave identical results, as did leaving the CH_2Cl_2 solution for only 5 min before removal of the solvent *in vacuo*. MS (Electrospray) *m/z* (%, fragment): 863 (100, M-CF_3SO_3).

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